A MODEL OF SOIL ORGANIC MATTER QUALITY
UNDER ANAEROBIC CONDITIONS
IN ARCTIC AND SUBARCTIC SOILS

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Abstract

The extent of anaerobic respiration by soil microbes is dependent on many factors, including water and nutrient availability, pH, temperature, oxidation/reduction potential, and soil organic matter quality. An understanding of the influence of these factors on anaerobic respiration is important as carbon dioxide (CO_2) and methane (CH_4) can act as greenhouse gasses. This study investigated the relationship between soil organic matter (SOM) and anaerobic respiration potential in arctic and sub-arctic soils. A model was developed to describe the dependence of anaerobic gas production on SOM properties. The model was generated by correlating SOM properties to anaerobic gas production for a suite of soils collected from the U.S., Canadian, and Scandinavian Arctic and Subartic. The SOM properties were characterized using pyrolysis-gas chromatography/mass spectrometry. The anaerobic gas production was measured using laboratory incubations. This model was then applied to soil samples taken from the Smith Lake Methane Flux Site at the University of Alaska Fairbanks in order to predict the anaerobic respiration gas production potential from soils in this area. Maps were constructed showing the predicted amount of anaerobic respiration within a 0.75 mile radius of the Smith Lake Methane Flux Site.

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Introduction

The Arctic has an important role in global carbon (C) budgets because of the large quantities of C stored in permafrost (Michaelson et al., 1996). It is estimated that northern ecosystems have accumulated 25-33% of the world's soil C (Oechel & Vourlitis, 1995). Gorham (1991) observed that wetland soils are primarily a sink of CO_2 because assimilation through plant photosynthesis generally exceeds release through decomposition of plant litter. On the other hand, wetlands are generally a source of CH_4 (Moore and Dalva, 1997). Methane is of concern to modern scientists because it is a greenhouse gas that is about 21 times as radiatively active as CO_2, and has increased in atmospheric concentration by about 1% per year during the last century (Steele et al., 1992). Almost 80% of the methane in the atmosphere was produced by anaerobic decomposition of organic matter (Winegardner, 1996). Wetlands thus play a role in the atmospheric regulation of these two gasses. Soil carbon (C) in the northern hemisphere is important to the global carbon cycle because of the preponderance of wetlands between 50 and 70°N. High latitude wetlands are responsible for nearly one-third of the global CH_4 derived from wetlands (Reeburgh, 1996). Northern wetlands are estimated to produce up to 10% of the global CH_4 emissions from natural sources (Fung et al., 1991).

Soil organic matter (SOM) is composed of a complex mixture of decayed plant and soil matter, and the polymeric arrangements produced by the random combinations of these materials with other organic substrates (Wilson et al., 1983). The different compounds in SOM have differing degrees of resistance to biological attack (Dai, 2001, Dai et al., 2002; White et al., 2002). Because of these differences, SOM in two soils will decompose at different rates. SOM composition can be analyzed using an analytical technique called pyrolysis-gas chromatography/mass spectrometry (py-GC/MS). Py-GC/MS has been used to characterize SOM in numerous other studies, including the characterization of SOM in arctic and antarctic soils by White and Beyer (1999) and Dai et al. (2002). Previous research found the relative abundance of numerous compounds in the SOM of a suite of tundra soils to be well correlated with aerobic respiration from these soils under substrate limiting conditions. It was found that SOM quality was

strongly correlated to aerobic respiration, while SOM quality was only weakly correlated to percent organic matter and uncorrelated to geographic origin (White et al., 2002).

Soil carbon can be degraded under aerobic or anaerobic conditions. The degradation of SOM in either condition is dependent on many biological controls, including nutrient availability, temperature, oxidation/reduction potential, and SOM quality. Northern ecosystems, and northern wetlands in particular, often have developed organic soils due to the slow decomposition of organic matter (Yavitt et al., 2004). The main factors leading to slow decomposition in northern ecosystems are unfavorable environmental conditions, such as cold, acidic peat, and a deficiency of resources, such as readily decomposable substrates and nutrients (Yavitt et al., 2004). A thorough understanding of the controls on SOM degradation is required to understand the current global carbon cycle and be able to predict future changes.

Microorganisms can be broadly categorized according to the terminal electron acceptor used. The terminal electron acceptor in aerobic metabolism is oxygen. A variety of different electron acceptors can be used in anaerobic metabolism, including sulphate, iron, carbon dioxide, and organic molecules. The microorganisms that dominate at the lowest redox potential are methanogens. Methanogens oxidize a limited number of simple compounds thereby creating methane as a waste product. Methanogens can oxidize H_2 and CO_2, acetate, formate, methylated compounds, and primary and secondary alcohols. Acetotrophy and CO_2 reduction by H_2 are the most common methanogenic pathways (Mer and Roger, 2001). Methanogenic fermentation of more complex compounds requires synergy or syntrophy with other organisms. Five orders and more than sixty species of methanogens are known to exist (Mer and Roger, 2001) The three orders most commonly found in soil and peat are *Methanobacteriales*, *Methanomicrobiales*, and *Methanosarcinales* (Horn et al., 2003; Galand et al., 2003). The rate of methane production in soil by methanogens can be quantified through anaerobic incubation of soil samples (Horn et al., 2003; Sundh et al., 2000).

The type and quality of organic matter available as a substrate for microbial metabolism affects CH_4 emission (Mer and Roger, 2001). However, the specific

components of organic matter that affect CH_4 emission are not well understood. The goal of this project was to develop and apply a model to estimate the dependence of anaerobic gas production on SOM quality under substrate limiting conditions, in arctic and sub-arctic soils. This goal relied on the hypothesis that anaerobic gas production could be predicted using a small suite of molecules derived from SOM. The hypothesis was tested by correlating the fraction of specific compounds present in an index of compounds to the measured anaerobic gas production from these soil samples. The best correlations between anaerobic gas production and an SOM compound "fraction of index" were used as a model for the relationship between anaerobic gas production and SOM quality. This model was then used to predict the anaerobic gas production potential in five areas of differing vegetation near the Smith Lake Methane Flux Site at the University of Alaska Fairbanks. This research was meant to analyze only the affect of SOM quality on anaerobic gas production. The many other factors that affect the magnitude of anaerobic gas production, which have been previously studied, were not considered in this research.

Literature Review

Methods of Soil Organic Matter Characterization

Soil organic matter (SOM) refers to the sum total of all organic carbon-containing substances in soil (Schulten, 1993). In 1926, von Post and Granlund developed the traditional method used to describe the degree of soil organic matter (SOM) decomposition. This method is still used today (Nilsson and Bohlin, 1993; Moore and Knowles, 1990). This method classifies organic deposits based on genesis, the content of determinable plant remains, and some physical properties. This method is limited due to the lack a of consistency that results from different environmental and climatological conditions, as well as differences in flora in different communities. In addition, experience in the determination of macrofossils is required to accurately use the system.

The von Post (1926) system was modified by Troels-Smith in 1955. The Troels-Smith method can be used in the field for a semi-quantitative determination of the volumetric proportions of the main elements in soils. The Troels-Smith system defined the degree of humification the same way it was described by the von Post (1926) system: the degree of disintegration of the organic components of the soil. The Troels-Smith system involved the description of deposits based on physical properties, humicity, or the degree of decomposition of organic substances, and component parts. The measures for physical quality are the degree of darkness, the degree of stratification, the degree of elasticity, and the degree of dryness. The component parts are the proportion of 15 soil constituents such as moss, roots, clay, and plant fragments. For all three classes of parameters a scale of 0-4 is used for characterization. Zero describes the absence of the element concerned, and 4 the maximum presence.

Lundqvist (1926,1927) proposed a more detailed method of characterizing the components of SOM. This method involved microscopic analysis of peat solutions under x250 magnification, and the characterization of the peat into categories similar to those used in previous methods.

Aaby and Berglund modified the Troels-Smith system in 1986. Aaby and Berglund (1986) improved upon the Troels-Smith systems by creating a more detailed

procedure for classifying grain size, improving the symbol system, and adding additional symbols. Moore and Dalva (1993, 1997) used this modified system.

The United States Department of Agriculture Natural Resources Conservation Service currently uses a system of taxonomy in which three kinds of organic material are distinguished (USDA, 1999). The degree of decomposition in this taxonomic system is described by the percent of organic material that is present as fibers. The more highly decomposed the soil, the lower the fiber content. The three kinds of organic soils, fibric, hemic, and sapric, are related to the fiber content. Fibric, hemic, and sapric soils become progressively more decomposed from fibric to sapric, thus have a decreasing fiber content, an increasing bulk density, and a decreasing water content. A color scheme, soil plasticity, and characteristics when dissolved in sodium pyrophosphate are all used in this classification scheme.

Another method of soil organic matter analysis is through acid and base extraction. The substances obtained from soil by alkali extraction are called humic substances (Schulten, 1993). The fraction of humic substances which are soluble in dilute base and then can be coagulated by acidification are humic acids. The fraction of humic substances which remain in solution when the basic extract is acidified are fulvic acids. The humic fraction that cannot be extracted either by dilute base or acid is humin (Schulten, 1993). SOM can also be analyzed through sequential digestion followed by colorimetric analysis. Updegraff et al. (1995) estimated the proximate carbon fractions based on sequential digestion of dried, ground samples in methylene chloride, water, and H_2SO_4, followed by colorimetric analyses of the water and acid-extracts for polyphenols and carbohydrates. The residue remaining can be broadly described as lignin, and are generally the larger and more recalcitrant carbon components of soil organic carbon.

A more modern method of soil organic matter classification is the identification of soil organic matter compounds after pyrolysis followed by gas chromatography and mass spectrometry (py-GC/MS). Schulten (1993) used py-GC/MS and pyrolysis-field ionization mass spectrometry (py-FIMS) to develop an understanding of the specific compounds in SOM. Schulten (1993) found that the majority of volatile pyrolysis

products between 300 and 600°C are alkylbenzenes. These alkylaromatic moieties form a "sponge-like" network that can trap and bind more labile organic compounds. White and Beyer (1999) used py-GC/MS to identify an index of compounds from an assortment of common biochemical compounds that could be used to draw conclusions about the parent organic material for three Antarctic soils. White et al. (2002) used the same method to correlate the percentage of SOM compounds to aerobic gas production from a suite of arctic soils. White et al. (2004) further developed this method to find that SOM quality could be tied to vegetation cover type in arctic tundra ecosystems.

Laboratory Studies

Many studies have been conducted in which soil samples were incubated under anaerobic conditions in a laboratory. Different variables were isolated in different studies. Many studies were conducted in which the effect of temperature on anaerobic laboratory incubations was investigated. Yavitt et al. (1988) performed anaerobic incubations of soil samples taken from bogs in the Appalachian Mountains in West Virginia and Maryland. Soil samples were taken throughout the year. Incubations for each sampling date were conducted at two temperatures, 19°C and the ambient temperature in the field at the time of sampling. It was found that the maximum rates of methane and carbon dioxide production in the surface peat of each plant community, in the incubations conducted at 19°C, occurred from November to April. However, the maximum rates of methane and carbon dioxide production in the incubations conducted at ambient field temperature occurred in midsummer, coinciding with maximum peat temperature. Yavitt et al. (1988) concluded that the maximum potential for methane and carbon dioxide production in surface peat from the Appalachian peatlands sampled exists in winter and early spring, but low temperatures at these times of the year constrain microbial activity. Yavitt et al. (1988) also found when the same experiment was conducted with soils from 30-35cm an increased temperature of 19°C had little effect on the rate of methane and carbon dioxide production.

Moore and Dalva (1993) found that differences in water table position, temperature, and peat type all significantly altered CO_2 and CH_4 emissions from the peat

($P < 0.05$). This study found that emissions of CO_2 and CH_4 increased by 2.4 and 6.6 times, respectively, when the incubation temperature was raised from 10°C to 23°C. Moore and Dalva (1997) conducted incubation at room temperature for 5 days, resulting in an average CO_2 production rate of 0.52 mg CO_2 g^{-1} d^{-1} in anaerobic conditions and 1.0 mg CO_2 g^{-1} d^{-1} in aerobic conditions.

Significant microbial activity occurs in some soils at subzero temperatures, although the magnitude of the response is highly soil dependent (Clein and Schimel, 1995). Rivkina et al. (2004) performed incubations of Siberian permafrost soils at different temperatures in order to discover the effect of melting of permafrost soils during climate change. Some of the permafrost soils had been frozen for millions of years. Incubations were conducted at temperatures between 5 and –16.5°C with $H^{14}CO_3^-$ and $^{14}CH_3CO_2^-$ as substrates. Methane formation from supplied radiolabeled substrates was found to be as high as 0.02 μmol CH_4 kg^{-1} day^{-1} at a temperature of –1.8°C. The temperature below which activity ceases varies among soil types (Hobbie et al., 2000). The rate of methane formation was reduced 2-fold over the temperature range 5 to -1.8°C. The most active sample had a drastic reduction in CH_4 production with a reduction of temperature; production at -16.5°C was 100-fold less than production at –1.8°C. This sample produced CH_4 at a rate only one order of magnitude lower than incubation of modern peaty tundra soils, and was the only sample studied that showed a high rate of methane production at –16.5°C. The other samples did not produce any CH_4 during incubation.

Laboratory incubations have also been used to study the effects of substrate quality on anaerobic soil decomposition. When comparing methane and carbon dioxide production among areas with differing vegetation cover in the Appalachian Mountains, production was found to vary 6.0 and 2.8 fold, respectively. CO_2 production rates were 2.1 – 13.0 times larger than CH_4 production rates. CO_2 production rates were estimated to be 30.6 – 79.0 mol m^{-2}, and CH_4 production rates were 2.7 – 17.5 mol m^{-2}. The *Sphagnum*-bog community sampled was found to generate the lowest amount of methane, while the *Sphagnum*-forest and sedge-meadow plant communities had the

highest amount of methane and carbon dioxide production. Yavitt et al. (1988) concluded that the *Sphagnum*-forest and sedge-meadow plant communities had increased anaerobic gas production due to lateral water movement that increased substrate availability or decreased toxin accumulation.

Moore and Dalva (1993) performed laboratory incubations of peat samples collected from a subarctic fen, a temperate bog, and a temperate swamp in Canada, as well as aerobic and anaerobic incubations of peat slurries. The incubation columns of peat were saturated with water and sealed for 30 days prior to the start of the experiment. Little difference was found between the productivity of samples collected from a 0-10cm depth and those collected from a 30-40 cm depth. The average quotient of aerobic:anaerobic CO_2 productivity over 5 day incubation periods was 1.3. The productivity of the three sample locations generally was found to be in order of bog>fen>swamp. Moore and Dalva (1997) expanded on their earlier work by performing aerobic and anaerobic incubations of many soil samples collected from bogs, fens and swamps in boreal, subarctic and temperate regions of Canada. Moore and Dalva (1997) found that soil origin was related to anaerobic CO_2 production in that soils from areas with predominantly bryophyte vegetation litter produced more CO_2 than soils of herbaceous origin, and soils of herbaceous origin produced more CO_2 than ligneous soils. Aerobic and anaerobic CO_2 production rates were strongly correlated (0.581) and anaerobic CH_4 production was positively correlated with CO_2 production (0.36). CO_2 production rates were greatest in the upper part of the peat profile. Anaerobic incubation of these soils resulted in an average CH_4 production rate of 3.1 $\mu g\ CH_4\ g^{-1}\ d^{-1}$. Average anaerobic CO_2 production during the 5-day incubation period was 161 times larger than CH_4 production.

Moore and Knowles (1990) performed laboratory incubations of soils from subarctic fens, temperate swamps, and temperate bogs in Quebec, Canada. They found that rates of methane production were generally highest in the surface layer (from 0-25 cm), and that production was highest in fens and lowest in bogs. Rates of methane production were generally found to decrease with depth, although in a few of the samples

studied, the CH_4 production in lower horizons was found to be larger than that of the upper horizons. When comparing samples with different degrees of decomposition, Moore and Knowles (1990) concluded that the degree of decomposition is not a good indicator of the relative rates of methane production and emission. This study illustrated that CH_4 emission is dependent on many variables.

Magnusson (1993) found that the mean CO_2 production rates in mineral soils with low organic matter content were similar in anaerobic and aerobic incubations; however, in organic soils the CO_2 production rate was 10 times greater under aerobic than anaerobic conditions. The correlation coefficient (r) between aerobic and anaerobic production rates was found to be 0.98. The ratio of aerobic to anaerobic activity was found to be 14 for organic soils and 2.9 for mineral soils. Some mineral subsoils were found to have anaerobic activity that was equal to or greater than aerobic activity. Mineral and organic samples incubated anaerobically both showed a decline in CO_2 production rates with increasing time of incubation, with the rates after 19 weeks of incubation being about 10% of the initial rates. When the incubation vials were flushed with N_2 gas the CO_2 production rate increased, leading to the conclusion that inhibitory substances cause a decrease in CO_2 production as the period of incubation increased. Methane production rates increased throughout the incubation period, but overall anaerobic activity decreased throughout the incubation period. The temporal decline in anaerobic activity was explained by a possible decrease in availability of energy substrates and reducible substances, and the accumulation of inhibitory agents. Respiratory activity was found to be higher during the first measurement period compared to later stages under both aerobic and anaerobic conditions, especially in mineral subsoils. This was attributed to disturbances of the microbial community and its substrates during sampling.

Updegraff et al. (1995) studied the relationship between SOM quality and methane production by performing 80-week aerobic and anaerobic incubations of three wetland soils. The soils were collected from a meadow, and the surface and subsurface horizons of a bog in Minnesota. The soil substrate quality was found using sequential

digestion followed by colorimetric analysis, as previously described. The incubations were conducted at both 15° and 30°C. The nitrogen mineralization rate, carbon mineralization rate, the partition of carbon between CO_2 and CH_4, the pH, and the Eh were measured throughout the incubation. Updegraff et al. (1995) found that the responses of nitrogen mineralization, carbon mineralization, and trace gas partitioning to both temperature and aeration depended on soil substrate quality. Sedge meadow soil had the highest nitrogen and carbon mineralization rates as well as the highest methane production rates under anaerobic conditions. The most variation in nitrogen and carbon mineralization was explained by differences in the size and kinetics of a small labile pool of compounds. The kinetics of this pool were more sensitive to changes in temperature and aeration than the large recalcitrant pool. Total C and N mineralization was positively correlated with the fraction of labile elements, and methanogenesis was negatively correlated with the fraction of recalcitrant compounds. Updegraff et al. (1995) concluded that climate change estimates must take care to account for the local variation in soil substrate quality and wetland type.

Laboratory incubations have also been conducted in order to analyze the effect of water content on soil decomposition. Moore and Dalva (1993) found that when the water table depth in the incubation column was reduced by half, the CO_2 emission rate increased by 4.3 times and the CH_4 emission rate decreased by 5.0 times. CO_2 emission was related to water table depth by a positive linear correlation, whereas CH_4 emission was related to water table depth by a negative logarithmic relationship. Hysteresis effects were found in both CO_2 and CH_4 emissions with respect to changes in water table depth.

Williams and Crawford (1984) conducted anaerobic incubations of peat from a transitional fen in Minnesota. Surface peats (10-25 cm) were found to produce an average of 228 nmol of CH_4 per gram dry weight, at 25°C and pH 4. Generally CH_4, production was found to decrease with increasing depth, although some deeper soil sections were found to produce more CH_4 than overlying soil layers. Methane production was found to be temperature dependent in surface soils, but not in peat from deeper soil layers. Maximal CH_4 production from deeper layers was found to occur at 12°C. Methane

production was also found to be pH dependent, with the optimum pH for maximum CH_4 production to be pH 6. Williams and Crawford (1984) experimented with the effect of chemical additions on the rate of CH_4 production. Glucose and carbonic acid were found to increase CH_4 production, acetate was found to inhibit CH_4 production, and cysteine-sulfide, nitrogen-phosphorus-trace metals, and vitamins-yeast extract did not affect CH_4 production.

Bergman et al. (1999) performed laboratory incubations of acidic surface peat from a boreal mire under conditions of varying temperature, pH, and substrate addition. The vegetation at the mire was predominantly *Sphagnum majus*. The rate of glucose degradation increased with both increased temperature and pH, under both aerobic and anaerobic conditions. Addition of glucose and starch increased production of CH_4 and CO_2 under both aerobic and anaerobic states, indicating that conditions were substrate limiting. However, the rate of anaerobic CH_4 production was not directly related to glucose degradation, whereas anaerobic CO_2 was tightly coupled to glucose degradation. Due to the production of ethanol, Bergman et al. (1999) concluded that yeasts or fungi were present in the peat in addition to methanogens. The CH_4 production rate decreased when the pH was raised from 4.3 to 6.2. Bergman et al. (1999) concluded that this occurred because of the accumulation of toxic undissociated volatile fatty acids. The aerobic:anaerobic CO_2 production ratio was 4.3.

Boon and Mitchell (1995) performed a study in which field and laboratory incubations of sediment were performed from a highly productive freshwater wetland on a floodplain in Australia. The *in-situ* CH_4 emissions were found to be highly temperature dependent, with maximal emission at 30-40°C; CH_4 emissions from the wetland were less than 0.01 mmol m^{-2} h^{-1} in winter and 2.75 mmol m^{-2} h^{-1} in summer. Methanogenesis accounted for 60% of the carbon flux from the *Eleocharis sphacelata* beds in this wetland, 30% of the flux from *Myriophyllum* sp. beds, and 40% of the flux from *Vallisneria gigantean* beds. Incubations were conducted with the addition of sulfate, nitrate, and molybdate, and by the cellulose azure method in order to study cellulose degradation rates. Nitrate inhibited CH_4 production, indicating competition between

methanogens and denitrifying bacteria. However, the incubations did not indicate competition between methanogens and sulfate-reducing bacteria. Ferric ion inhibited in vitro methanogenesis, causing a 16-49% reduction in CH_4 production during the summer season. Acetate, cellulose, starch, and aquatic plant matter increased *in-vitro* methanogenesis, indicating a substrate-limiting environment. However, no relationship between methane emissions and benthic cellulase activity could be found in the field.

A study by Billings et al. (2000), also conducted on a floodplain, found that areas of methane emission and methane uptake were both present, and that a decrease in precipitation decreased methane uptake. The methane uptake ranged from –0.02 to 0.57 mg m^{-2} day^{-1} in the floodplain site at the Bonanza Creek Long Term Ecological Research Site in interior Alaska.

Mishra et al. (2003) performed a study in which the effect of SO_4^{2-}, Cl^-, and HCO_3^- on anaerobic CH_4 production was investigated. Laboratory incubations were conducted on alluvial soil from India. The test incubations were amended with a saline solution containing the specific ion being tested in a quantity necessary to raise the pore water electroconductivity to 8 dS m^{-1}. It was found that SO_4^{2-} was the most inhibitory anion to CH_4 production, followed by a combined salt mixture of sulphate, bicarbonate, and chloride. Salinity amendment did not affect soil redox potential or soil pH. Readily mineralizable carbon content differed significantly among the different treatments. Acetotrophic methanogens were lowest in Cl^- amended soils, followed by SO_4^{2-} amendment; little or no changes were found with bicarbonate amendment. Mishra et al. (2003) concluded that inhibition of methanogenesis by salinity is significant, and that SO_4^{2-} inhibition may be due to competition.

Brown et al. (1989) performed incubations of peat from Ottawa, Ontario, Canada. Ten-fold more methane was found to be produced in incubations of surface peat than subsurface peat, although in the field it was found that subsurface peat produced more methane than surface peat. Laboratory incubation of peat from three subsurface levels (60 cm, 90 cm, and 120 cm) produced an average of 2.68 nmol CH_4 g^{-1} dry weight h^{-1} (range of 0.80 to 5.28 nmol CH_4 g^{-1} h^{-1}). The 90 cm depth was found to produce more methane

than the 60 and 120 cm depths, 3.49 nmol CH_4 $g^{-1}h^{-1}$, 1.75 nmol CH_4 $g^{-1}h^{-1}$, and 2.82 nmol CH_4 $g^{-1}h^{-1}$, respectively. Laboratory incubations of surface peat produced 39.9 nmol CH_4 $g^{-1}h^{-1}$, ranging from 2.02 to 62.7 nmol CH_4 $g^{-1}h^{-1}$. There was found to be little correlation between cellulose content, acid-soluble lignin, or residue and either incubated or extracted methane production. There was also little correlation between the amount of methane extracted at different subsurface depths and the amount produced during laboratory incubation of peat from these levels. The pH was found to increase with depth.

Methanogens can maintain their populations under extraordinarily unfavorable conditions (Rivkina et al., 2004; Mer and Roger, 2001). Methanogens and methanotrophs were found simultaneously in both oxic and anoxic sections of ricefields (Mer and Roger, 2001). Methanogenesis has been well documented in acidic environments (Svensson and Rosswall, 1985; Williams and Crawford, 1985; Svensson, 1984). Williams and Crawford (1985) isolated a strain of methanogen of the family *Methanobacteriaceae* that was acid tolerant. This strain was able to produce methane at pH 3.1, although no growth was visible at a pH below 5.3.

Field Studies

Two main factors that can reduce the decomposition rate of SOM are an unfavorable environment and a deficiency of resources (Yavitt et al., 2004). Unfavorable environmental conditions that often exist in northern climates are cold temperatures and low pH values (Yavitt et al., 2004; Bubier et al., 1993), which are part of the cause of the large carbon storage in northern soils (Hobbie et al., 2000). Hobbie et al. (2000) concluded that temperature, topography, and vegetation composition are the primary controls on litter decomposition at the regional scale. Hobbie et al. (2000) also concluded that cold temperature is the most important climatic control on litter decomposition at high latitudes. Torn and Chapin (1993) found that although areas of differing vegetation on the north slope of the Brooks Range in Alaska had different CH_4 emission rates, within each vegetation type differences in soil temperature and moisture explained 75% of the variance.

Methanogenesis is optimum between 30 and 40°C, both due to optimum activity of the methanogen population and the increased activity of the symbiotic organisms that precede methanogens in soil fermentation (Mer and Roger, 2001). However, Giardina and Ryan (2000) refute the theory that decomposition is temperature dependent with data showing that decomposition rates from 82 sites around the world do not correlate with temperature.

A number of studies have been conducted to examine seasonal and daily temperature variations on CH_4 emissions. Boon and Mitchell (1995) found that the *in-situ* CH_4 emissions from a highly productive freshwater wetland in the floodplain in Australia were highly temperature dependent, with maximal emission at 30-40°C; CH_4 emissions from the wetland were less than 0.01 mmol m^{-2} h^{-1} in winter and 2.75 mmol m^{-2} h^{-1} in summer. Similarly, Goulden et al. (1998) found that an increase in soil respiration in central Manitoba, Canada, during the late summer was linked to the thawing and warming of deep humified organic matter.

Although most studies found negligible CH_4 production in winter months (Boon and Mitchell, 1995; Vourlitis et al., 1993, Yavitt and Lang, 1988), Huttunen et al. (2003) found significant winter CH_4 production in a eutrophied boreal lake in Finland. Huttunen et al. (2003) measured gas ebullition and CH_4 accumulation in the water column after ice cover formation in the winter. Winter CH_4 production was 3.6 – 7.9 g m^{-2}, all of which was released during snowmelt. The winter CH_4 production from the pelagic zone of this lake was estimated to account for 22 - 48% of the annual CH_4.

Soil mass and nitrogen content decrease during the course of the winter in the Arctic; This may be due to spring leaching and/or microbial decomposition (Hobbie and Chapin, 1996). A study of winter soil respiration found that much of the CO_2 produced was derived from organic matter that was more than 50 years old, indicating that winter soil decomposition is predominantly a factor in deeper soils that are often warmer than soil surface temperatures (Winston et al., 1997). Hobbie et al. (2000) concluded that winter CO_2 fluxes are substantial in annual carbon budgets and likely influence both the magnitude and direction of annual carbon fluxes. Winter microbial decomposition may

be dependent on the amount of unfrozen water that remains in frozen soil because microbial activity can occur in films of liquid water that remain on soil particles even after the bulk of the water has frozen (Hobbie et al., 2000). Winter microbial decomposition may also be dependent on soluble material remaining in water films deep in the soil profile, instead of on non-dissolved soil components (Clein and Schimel, 1995). Hobbie et al. (2000) suggest that substrate use may change as the temperature drops, favoring substrates that can be metabolized with minimal enzyme activation energy requirements.

Another unfavorable condition often present in northern climates is acidic soil pH values. However, although methanogenesis is generally increased in neutral environments, methanogens have been known to adapt to acidic environments (Mer and Roger, 2001). Methanogensis in some acidic peat environments areas was found to be optimum between pH 5.5 and 7.0 (Mer and Roger, 2001).

Methanogenesis may be limited if inadequate amounts of readily decomposable substrates or necessary nutrients are present in the soil (Yavitt et al., 2004). Necessary nutrients for microorganisms include N, P, Mg, Fe, Co, Ni, and Mn. (Yavitt et al., 2004). It has been found that active Mn is positively correlated with methanogen and methanotroph densities (Mer and Roger, 2001). Methanogenesis has been found to be generally lower in sulphate rich soils, due to competition with sulphate reducing bacteria (Mer and Roger, 2001). Nilsson and Bohlin (1993) found that soil water CH_4 concentration was related to nickel, sulphur, calcium, sodium, and potassium concentrations.

Yavitt et al. (2004) studied the relationship between unfavorable environmental conditions and resource deficiency on SOM decomposition by transplanting four peat soils with different chemical compositions into six sites with different environmental conditions. Yavitt et al. (2004) found that a large CH_4 production (4000 nmol $g^{-1}d^{-1}$) correlated with large holocellulose content, large concentrations of non-methoxyl substituted p-hydroxyl phenolic compounds, and low concentrations of N, Ca, and Mn. CO_2 production was found to be positively correlated to holocellulose content and

negatively correlated to N concentrations, regardless of the transplant site. Low CH_4 production rates were found to be related to a large ratio of vanillic acid to vanillin aldehyde among mono-methoxyl substituted V-phenols.

Substrate quality is just as important as temperature in explaining variation in decomposition rates in arctic and boreal regions (Hobbie et al., 2000). Mer and Roger (2001) state that the decomposition rate for submerged soils is dependent upon the type of material being decomposed, the availability of electron acceptors, and the presence of microbial populations. A positive correlation has been found between soil organic matter content and methanogenic potential (Mer and Roger, 2001). Methane production generally decreases when the C content and the C/N ratio of the soil decreases (Mer and Roger, 2001). Methane production also generally decreases with increased lignin concentrations and low concentrations of soluble carbohydrates (Hobbie, 1996). Lower soil horizons generally have slower decomposition rates than fresh litter due to the accumulation of recalcitrant compounds, the formation of recalcitrant compounds, and cold temperatures (Hobbie et al., 2000). The accumulation of recalcitrant compounds in soil can be caused by the faster decomposition of labile compounds; recalcitrant compounds can be formed by humification and fire (Hobbie et al., 2000). One study found that 70% of methane production originates in the top 5 cm of the organic horizon, indicating that recent plant remains are an important factor in methanogenesis (Mer and Roger, 2001). However, Tolonen and Turunen (1996) found that the stores of carbon in deep humified soil horizons are so large that, even at slow rates of decomposition, they may produce significant quantities of carbon dioxide.

There have been a number of studies of the decomposition rate of fresh litter in the soil organic horizon. Hobbie and Chapin (1996) found that woody stems, mosses, lichens, and evergreen leaf litter decompose slower than deciduous and forb leaf litter. Flanagan and Van Cleve (1983) found that, in Alaskan taiga, birch forests decompose faster than spruce forests, due to both warmer temperatures in birch forest areas and better substrate quality in birch litter than in spruce litter.

Hobbie et al. (2000) found that the litter of deciduous species decomposed twice as quickly as moss litter, primarily due to the fact that moss provides poor substrate quality and low nutrient content for microorganisms, although it often thrives in poorly drained ecosystems, which also contributes to its slow decomposition rates. Additionally, *Sphagnum* species are known to produce compounds with antimicrobial properties (Verhoeven and Toth, 1995). Van Breemen (1995) found that the most common wetland plants, *Sphagnum* moss and ericaceous shrubs, are composed of hard to decompose organic compounds, and are nutrient poor. Nilsson and Bohlin (1993) found that soil water CH_4 and CO_2 concentrations were both positively correlated to the presence of *Sphagnum* remains, and negatively correlated to *Carex* remains, and concluded that this was most likely due to the fact that *Carex* peat contains much less cellulose and hemicellulose than *Sphagum* dominated peat, although differences in the hydrological flow pattern in the area may have contributed to the findings.

Studies have been conducted analyzing the effect of different soil properties on soil decomposition rate. Significant CH_4 production in wet peat soils is linked to organic matter with a particle size larger than 2.0mm (Mer and Roger, 2001). However, Hobbie et al. (2000) concludes that soil organic matter decomposition may be unrelated to soil texture in peaty soils. Another factor that may affect soil decomposition in northern soils is the effect of cryoturbation, which may cause organic matter from surface horizons to be pushed into lower horizons and stabilized in permafrost (Hobbie et al., 2000).

Studies have also been conducted analyzing the effect of ecological properties on soil decomposition rates. The presence of vegetation may be an important factor in aiding the transport of methane from the soil to the atmosphere (Mer and Roger, 2001). It has been found that wet tundra soil without vegetation emits less CH_4 than similar soils with vegetation, indicating that the vegetation serves as an important conduit for CH_4 transport (Torn and Chapin, 1993). Kelley et al. (1995) found large seasonal variations in methane emission rates across a tidally flooded bank margin of the White Oak River in North Carolina were linked to the cycle of growth and senescence of vascular plants.

Many studies have been done to measure the *in-situ* flux of methane from wetland and forest soils. Roulet et al. (1992) found that there was a daily flux of 0.38 to 56.3 mmol CH_4 $m^{-2}d^{-1}$ in boreal forest in eastern Canadian. Rask et al. (2002) measured the methane flux from a boreal wetland in central Saskatchewan, Canada, using a static chamber technique. Rask et al. (2002) found that methane fluxes at this site ranged from 176 to 2250 mmol CH_4 $m^{-2}yr^{-1}$. The daily fluxes in this region ranged from 1.08 to 13.80 mmol CH_4 $m^{-2}d^{-1}$. Rask et al. (2002) found that methane flux was directly correlated with water levels, P concentration, and temperature at all measurement locations except two in the central part of the fen, where there was water flow through the fen.

A similar study conducted by Bubier et al. (1993) in northern Ontario, Canada, using the static chamber method of measuring CH_4 flux, found that seasonal CH_4 fluxes ranged from 0.4 – 67.5 mg m^{-2} d^{-1} (0.06-10.1 g m^{-2} yr^{-1}). When these local fluxes were applied to the greater Clay Belt region in Ontario, Canada, Bubier et al. (1993) concluded that the annual CH_4 flux from this region is 3.4 g m^{-2} yr^{-1}. Bubier et al. (1993) also found that seasonal mean water table position explained most of the variability in the CH_4 emission among wetlands (r^2 = 0.74). The 15 sites used in this study were divided into three microtopographic regimes: hummock, hollow, and lawn. Methane fluxes from hollows were 5-60 times higher than in hummocks. The greatest difference in CH_4 flux between hummocks and hollows corresponded to areas with the greatest difference in water table position relative to the peat surface. Bubier et al. (1993) found that the open bog sites in this study showed large differences in CH_4 flux when dominated by hummocks and hollows.

Whalen and Reeburgh (1992) performed a study in which weekly net CH_4 flux was measured at arctic tundra sites in Alaska between 1987 and 1990. The average summer soil temperatures at the locations sampled ranged between 4 and 9°C. They found that there was a yearly methane flux of 119-1075 mmol CH_4 m^{-2} d^{-1} in Alaska, and that tussock:shrub and wet meadow tundra emitted about 42 $\pm$ 26 Tg CH_4 yr^{-1}. Coefficients of variation for CH_4 emission ranged between 67 and 118%. Tussocks (*Eriophorum*) are responsible for most of the CH_4 emitted from tussock:shrub tundra, and

Carex accounts for most of the CH_4 emission from wet meadow tundra. Negative fluxes were never found during this study. In general, highest fluxes were recorded in midsummer, and lowest fluxes were recorded in late winter. Winter flux characteristics were found to have no year-to-year consistency. Thaw season CH_4 emissions were found to account for between 77 and 95% of the annual emissions. However, emissions would have been greater than 90% at all locations sampled if the thaw season were considered to extend until soils froze to permafrost. Whalen and Reeburgh (1992) found that there were high within-site and spatial variations in thaw season CH_4 fluxes. They also found that CH_4 flux and subsurface properties were largely unrelated.

Many other studies have similarly found high CH_4 emission variability. Svensson and Rosswall (1984) found the standard deviation in methane emissions to range between 3 and 174% in wetlands in northern Sweden. An earlier study conducted by Whalen and Reeburgh (1990) similarly studied CH_4 emission from wetlands in Alaska. Whalen and Reeburgh (1990) found that coefficients of variation for methane emission from duplicate chambers at the same site averaged 51%. When the CH_4 fluxes were grouped by site type, they were lognormally distributed, and differences among means were statistically significant. Another study conducted by Whalen and Reeburgh (1992), found that although summer air temperatures and precipitation were roughly comparable in 1987-1989, there were differences in the site fluxes that they were unable to explain. Lessard et al. (1994) found high variations in rates of CH_4 uptake and CO_2 emission from Canadian cultivated and forested soils. Lessard et al. (1994) concluded that some sites required up to 452 static chamber measurements in order to obtain gas flux estimate with a 10% accuracy.

Moore and Knowles (1990) found that there was a yearly flux of 12.5 to 625 mmol CH_4 $m^{-2}yr^{-1}$ in the eastern Canadian subarctic, with a coefficient of variation between sites ranging from 0.23 to 2.0. There were up to two orders of magnitude difference in daily CH_4 emissions both within and between sites. It was found that, within a subarctic fen, variation in CH_4 emission was primarily controlled by the soil thermal regime. However, topography, spatial variability, and water table elevation were found to

be important controls on the variation between CH_4 emissions in different subarctic fens. Emission rates were found to be lower during the early summer and to reach peak values in the late summer and early autumn. Strong CH_4 emission was recorded during spring thaw, which was concluded to be a result of the release of methane produced during the winter and trapped within and beneath ice.

King and Reeburgh (2002) conducted a ^{14}C pulse labeling experiment under field conditions at Toolik Field Station in Alaska in order to estimate the contribution of recent plant photosynthates to CH_4 emission. The experiment was conducted by exposing mesocosms of wet sedge tundra (soil cores that contain soil and the surface vegetation) to $^{14}CO_2$ in stainless steel containers. The containers were left in the field during the course of the experiment to maintain realistic environmental conditions. The average CH_4 emission rate from the plant-soil mesocosm was 0.45 g C m^{-2} d^{-1}. The study found that carbon assimilated by plants via photosynthesis during the pulse labeling period turned over rapidly and was emitted as CH_4 within 24 hours. However, the contribution of recent photosynthates to total CH_4 emission was low. Less than 1% of the $^{14}CO_2$ taken up through photosynthesis was emitted as $^{14}CH_4$ during the two week study period.

Hirota et al. (2004) measured methane emissions from the Luanhaizi wetland, an area of alpine tundra on the Quinghai-Tibetan Plataeu, China. Static chamber measurements of CH_4 flux were made in four vegetation zones along a gradient of water depth. Four distinct plant zones were present: *Hippuris*-dominated, *Scirpus*-dominated, *Carex*-dominated, and *Potamogeton*-dominated. The smallest CH_4 flux was observed in the *Potamogeton*-dominated area, with a seasonal mean of 33.1 mg CH_4 m^{-2} d^{-1}. The greatest CH_4 flux was found in the *Hippuris*-dominated zone, in the second deepest area, with 214 mg CH_4 m^{-2} d^{-1}. CH_4 flux from three zones showed marked diurnal change and was found to decrease dramatically under dark conditions. Methane fluxes from all zones increased during the growing season with increasing aboveground biomass.

West et al. (1999) performed a similar study in alpine tundra in Colorado. West et al. (1999) studied the relationship between three areas of distinct vegetation types and the methane emission from these sites. In areas with a large winter snowpack, *Carex*

scopulorum dominated. In areas with a small winter snowpack, *Kobresia myosuroides* dominated. In areas with a moderate snowpack, *Acomastylis rossii* dominated. Plant productivity, SOM content, and methane emission were found to decrease from areas with large to areas with small winter snowpacks. CH_4 was correlated with temperature in the wet areas, whereas CH_4 oxidation was negatively correlated with soil moisture in the medium soil moisture areas and stimulated by precipitation in the driest areas.

Nilsson and Bohlin (1993) studied the relationship between soil water CH_4 and CO_2 concentrations and the botanical and chemical composition peat in soils from wetlands in northern Sweden. The concentration of CO_2 in the peat water tested ranged between 0.97 and 6.5 mM, and the concentration of CH_4 varied between 0.05 and 1.2 mM. Nilson and Bohlin (1993) found that CH_4 concentrations were correlated to depth with an explained variance (r^2) value of 0.63.

Models

Enquist et al. (2003) developed a model of ecosystem respiration based on the approximate rate of limiting resource supply, the rate of resource use by all individuals, temperature, and the total ecosystem biomass. This model, which is a complicated expression not shown here, found that ecosystem respiration is directly proportional to resource availability. This model was tested and supported by data collected from 19 CO_2 flux towers in North America and Europe.

Shindell et al. (2004) modeled methane emissions from wetlands using a GISS climate model incorporating linear parameterization derived from a detailed process model. The geographic distribution of wetlands was found to be climate dependent. Doubled CO_2 simulations using this model resulted in an increase in annual average wetland methane emissions from 156 to 277 Tg/yr, an increase of 78%. The bulk of this increase was due to enhanced emissions from existing tropical wetlands, although high northern latitude wetland areas expand and emissions nearly triple during the northern summer season. However, a model by Potter (2004) found that over the 1950-1999 climate record at Denali National Park the changing taiga ecosystems were net sinks for atmospheric CO_2 of about 1.3 kg C m^{-2}. During the warm 1990's these forests were

predicted to be net carbon sinks of more than 15 g C m^{-2} per year in 8 out of 10 years. Predicted net primary production for the forest continues to increase with a projected warming trend for the next 25 years at a mean rate of about +1.2 g C m^{-2} per year.

Other methods of modeling include the modeling methane flux using Fick's Law (Billings et al., 2000), multivariate analysis (Bohlin et al., 1989), and linear regression (Nilsson and Bohlin, 1993). Nilsson and Bohlin (1993) found that when CH_4 and CO_2 concentrations were correlated to depth, botanical composition, and degree of humification, the explained variance (r^2) values were 0.72 and 0.56, respectively. When chemical (Ni, S, Ca, K, and Na concentration) and physical variables were then added to the model describing CH_4 and CO_2 concentrations in soil water 75% of the CH_4 variance and 65% of the CO_2 variance was explained by these variables.

Methods and Materials

Laboratory Experiments

Twenty soil samples from twelve different locations and five different countries were chosen for anaerobic incubation. The locations of the sampling sites for these soils are shown in Figure 1. Fifteen of these soils were used in a White et al. (2002) study that modeled aerobic substrate quality based on SOM composition. The incubation was conducted on an aliquot of soil from each site containing 2 g of organic carbon. Water was added to achieve 70 ml total volume and neutralized with 1 M sodium carbonate. All samples were then filled to 100 ml total volume with a nutrient buffer containing mono and dibasic potassium phosphate, ammonium nitrate, and magnesium sulfate. A molar C:N:P ratio of approximately 100:3:1.5 was achieved, not including N and P originally present in the soil. A molar C:K:S:Mg ratio of 100:2.3:0.14:0.14 was achieved, not including nutrients originally present in the soil. The samples were then put in a 250ml amber glass bottles with septa, and incubated at room temperature (20°C) with constant shaking. The incubation was conducted for 8 weeks. The incubation as well as a replicate incubation of six soil samples (Council C soil) were conducted with the bottles upside down. The pressure increase caused by gas production was measured approximately biweekly. The pressure was measured using a Cole-Parmer digital pressure gauge.

The organic matter of these soils was analyzed using py-GC/MS. Pyrolysis was performed on a CDS Analytical Pyroprobe 2000/AS2500. The pyrolyzer was connected to an HP 6890 gas chromatograph (GC) in tandem with an HP 5973 mass selective detector (MSD) operated in electron impact (EI) mode. Compounds were separated in the GC using a Restek Rtx35-MS column (30 m x 0.32 mm x 0.25 μm). The pyrolysis interface temperature was held constant at 280 °C. The pyrolysis reaction chamber was programmed to ramp at 10°C/ms from the interface temperature to 700 °C and hold at 700 °C for 10s. The GC was run for 1 min with pulsed splitless injection at 25 psi with a temperature program of 40 °C for 30 min, ramp at 1 °C/min to 120 °C, ramp at 2 °C/min to 220 °C, and a final ramp at 10 °C/min to 280 °C and hold for 10 min to clean the column before the next run. The program was run with a constant 2.0 ml/min flow of

Site	# of samples	Collected By:
Barrow, Alaska	3	J. Strause, K. Yoshikawa
Fairbanks, Alaska	2	J. Strause, S. Carlson
Kogru River, Alaska	2	D. White
Lonely, Alaska	1	D. White
Teshekpuk Lake, Alaska	1	D. White
Ivotuk, Alaska	2	P. Overduin, D. White
Council, Alaska	4	C. Copass/ D. McGuire
Resolute, Canada	1	S. Howell/ K. Young
Longyearbyen, Svalbard	1	A. Killingtveit
Saltfjall, Norway	1	I. Ask
E. of Mo I Rana, Norway	1	I. Ask
Xingjiang, China	1	C. Ping

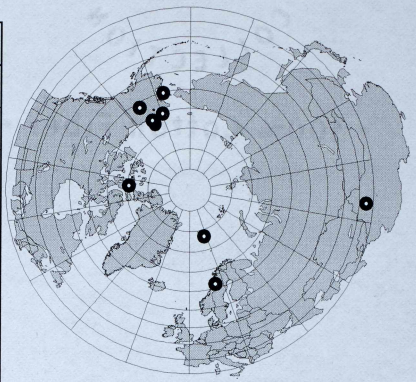


Figure 1: Table and map describing soils used in the incubations. The table lists the location, number of samples, and person who collected the samples. The polar projection map shows the location of these samples.

helium gas. Mass spectra were identified using the Wiley 275 library. Clean sample tubes were run every fourth sample to prevent and/or detect any carry over.

Thirty pyrolysis products were selected to constitute an index that could be related to anaerobic gas production. The index compounds were based on previous studies (White et al., 2002), and were broadly associated with the biochemical classes of primary and secondary polysaccharides, polypeptides, lignin, phenolic precursors, lipids, alkanes, naphthalene, and polycarboxylic acids. The pyrolysis products of each of the compound classes that were used to build the index are listed in Table 1.

For each sample, summing the abundance of all pyrolysis products associated with each class, and dividing by the total index abundance produced a "fraction of index" for each of the nine compound classes.

Table 1: Classes and compounds used to characterize SOM quality.

Pyrolysis Product	Compound Class	SOM source *
furfural	Primary Polysaccharides	Carbohydrates
hydroxyfuran		
methyl hydantoin		
1,4:3,6-dianhydro-ad-gluco		
methylfurfural	Secondary Polysaccharides	Carbohydrate origin presumed
2-propyl furan		
Indole	Polypeptides	Porphyrins, proteins, nucleic acids
Pyridine		
2-methoxyphenol	Lignin	Lignin
4-ethyl-2-methoxy phenol		
4-vinyl-2-methoxy phenol		
dimethoxy propenyl phenol		
phenol	Phenolic Precursors	Humic acids, lignin, proteins, polycarboxylic acids, carbohydrates
2-methyl phenol		
4-methyl phenol		
dimethyl phenol		
1-tridecene	Lipids	Fats and waxes
1-pentadecene		
1-hexadecene		
1-heptadecene		
1-octadecene		
decane	Alkanes	Fats and waxes
undecane		
dodecane		
tridecane		
pentadecane		
hexadecane		
naphthalene	Naphthalene	Naphthalene
methylcyclopentanone	Cyclopentenones	Aliphatic polycarboxylic acids
dimethylcyclopentanone		

*Cited from Wilson et al. (1983) and Bracewell et al. (1989).

The CH_4 and CO_2 content of the gas in the incubation headspace was subsampled using a 50µl gas-tight syringe and quantified using a Gow-Mac Series 550 gas chromatograph equipped with a thermal conductivity detector. Gas chromatography was performed on 25 µl of gas from each incubation vessel, after each pressure measurement.

A mole fraction of the number of moles of CO_2 or CH_4 compared to the number of moles of both gasses present was found.

The total number of moles of CH_4 and CO_2 produced was found by applying the ideal gas law to the increased pressure in the incubation vessel, resulting in the number of moles of both gasses produced. The molar volume of other gasses produced, such as hydrogen sulfide, was assumed to be insignificant. The mole fractions of CH_4 and CO_2 were then used to find the number of moles CH_4 and CO_2 in the total number of moles produced. The rate of anaerobic gas production was compared to the rate of aerobic gas production in these soil samples found by White et al. (2002).

Model Development

For each measurement of incubation pressure, a linear correlation coefficient (R) between the incubation pressure and the fraction of index for each SOM compound class was calculated. A linear model was then constructed based on the best correlation that related SOM composition to anaerobic gas production.

Model Application: Site Description

The sampling sites selected to apply the model were located at the University of Alaska Fairbanks Smith Lake Methane Flux Site. Fairbanks is located in interior Alaska at coordinates 64°N and 147°W. Fairbanks is an area of discontinuous permafrost. The mean maximum July temperature in interior Alaska is 22°C. In winter the lack of sunshine permits the temperature to drop to –48°C. Average January minimums in this area are 28°C.

Five areas of different vegetation types were sampled: tussock, trough, and low, medium, and high-density spruce forest. An aerial photograph of the Smith Lake Methane Flux Site is shown in Figure 2. Photographs illustrating the vegetation at these sites are shown in Figure 3. All five vegetation areas are located on permafrost. The tussock vegetation area consists of dense masses of grasses. The troughs were filled with water in the summer and ice in the winter. The troughs were relatively free of live vegetation. The low-density black spruce forest vegetation area consisted of small black spruce trees, small shrubs, and a dense mat of lichen and moss undergrowth. The medium

density black spruce forest vegetation area consisted of sapling black spruce trees, seedling aspen and birch hardwood trees, blueberry bushes and small shrubs, and lichen and moss undergrowth. The high-density forest vegetation area consisted of large spruce and hardwood trees with minimal undergrowth.

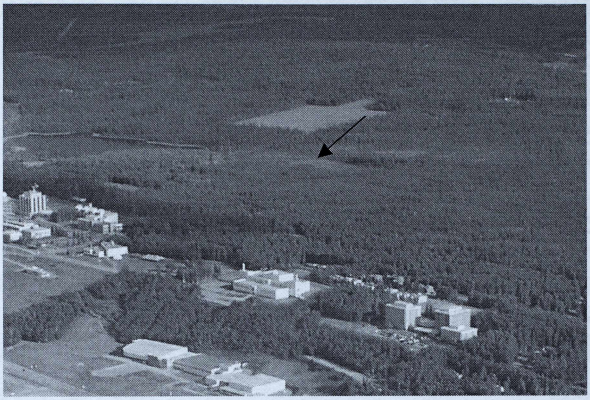


Figure 2: An aerial view of the Smith Lake Methane Flux Site. The arrow shows the location of the site.

The density of spruce and hardwood trees in each forest vegetation area is shown in Figure 4 below. These values were found by counting the trees present in a 10m by 10m area. Although not quantified, visual inspection of the trees at the different forest vegetation areas found that the average height and diameter of the trees increased with increasing density.

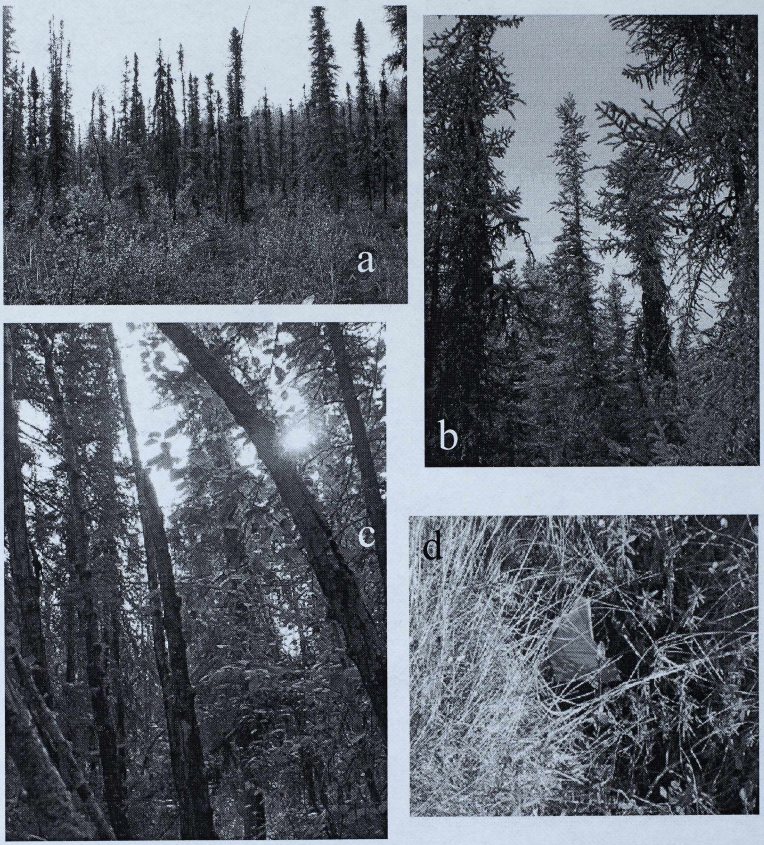


Figure 3: Photographs of the vegetation areas sampled near Smith Lake in Fairbanks, AK. a) Low density black spruce forest. b) Medium density black spruce Forest. c) Dense black spruce and hardwood forest. d) Tussock and trough.

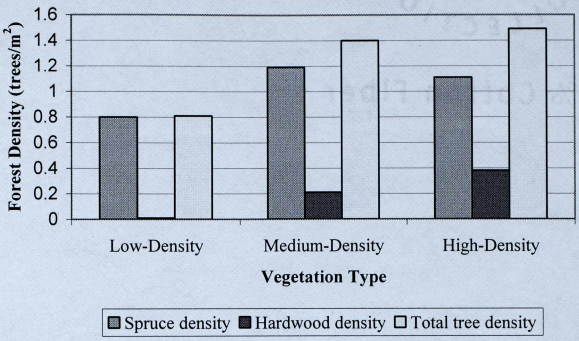


Figure 4: Forest density measurements of low, medium, and high-density forest sampling sites.

Model Application: Methods

The tussock, trough, and low-density vegetation areas were sampled in the summer season of 2003. Medium and high-density forest vegetation areas were sampled in the summer of 2004. These areas were sampled approximately every other week starting in early June until the ground froze in September. The areas were sampled by taking soil cores to the depth of thaw. The depth of thaw was recorded when the soil cores were taken. Soil cores taken were separated into organic (O), A, and B horizons. The A and B horizons were then further separated into sections. The sections were stored frozen until analyzed by py-GC/MS. The lower sections of the medium and high-density forest vegetation soil cores had very low concentrations of organic matter and were not analyzed due to difficulty in obtaining accurate results using these methods.

The models relating anaerobic gas production potential to SOM quality were then applied to soil samples collected from the five areas of differing vegetation near Smith Lake in Fairbanks, AK throughout the summers of 2003 and 2004. Application of the model resulted in a numerical value for the number of moles of gas produced during a certain time period. The number of moles of gas produced does not reflect the amount of gas that is, or would be, expected to be produced under normal field conditions because

the conditions used in the incubation did not resemble typical field conditions. The numerical value resulting from model application was used to compare anaerobic gas production potential from soils of differing substrate quality. This value was matched to a color scheme, and displayed on graphs showing the estimated anaerobic gas production for each soil core section. Maps were then constructed by coloring the different vegetation areas on a photograph using Adobe Photoshop. The average estimated anaerobic gas production from each vegetation area on each sampling day was found by averaging the estimated anaerobic gas production value the soil sections of each soil core. These areas were then colored in using the color scheme to show the relative potential of anaerobic gas production.

Error Analysis

The experimental error in this study was analyzed using two separate experiments. Six replicate incubations of soil from Council, Alaska (Council C) were performed in order to quantify experimental error associated with the incubation. The 95% confidence interval was found for each measurement point.

The sampling error and site heterogeneity was analyzed by taking five replicate soil cores on that same sampling date in the low-density black spruce vegetation area. The replicate soil cores were taken 10cm from the adjacent core in order to imitate methods used in the seasonal sampling of the three forest vegetation areas. These soil cores were broken into O and A horizon sections. Py-GC/MS was conducted on the soil sections, and the developed model was applied to the SOM content. The 95% confidence interval was then found for the O and A horizon sections.

Results

Laboratory Experiments

The pressure in the incubation bottles ranged from 0 to 4.90 psi during the incubation period. Figure 5 shows the average cumulative pressure versus week of measurement for all the samples. Individual graphs of incubation pressure versus week for the each sample are shown in the Appendix A, Figures A3-A21. Most incubation samples exhibited a sharp increase in pressure during the first two weeks of incubation, followed by a slow increase in pressure for the duration of the incubation. The standard deviation from the average pressure was 1.4 psi during the second week of incubation. The standard deviation increased throughout the incubation to 1.6 psi during the eighth week of incubation. These large standard deviations indicate that there were large variations between samples.

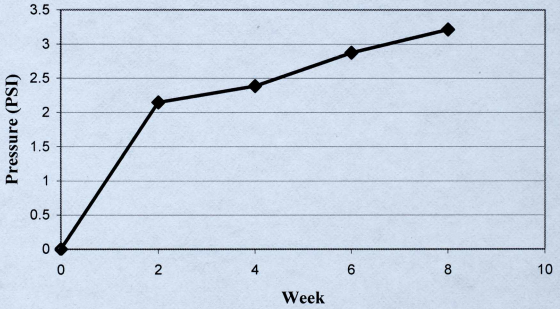


Figure 5: Average cumulative incubation pressure versus week of incubation.

Incubating the bottles upside-down ensured that there was no loss of air through the pierced septa. Unfortunately, the inverted incubations caused the septa to be covered with water and dirt from the soil. As a result, pressure gauge needles were sometimes clogged during measurement. Inaccurate pressure measurements were partially resolved by using alternative minimum values to report the pressure measurements. If the pressure measured in the bottle decreased from the week before, an alternative minimum value

was reported. The alternative minimum, in this case, was the previous week's measured value. All actual and alternative minimum pressures are reported in Table A2.

The SOM indices of the incubated soils were found through py-GC/MS. The average fraction of index for each compound class is shown in Figure 6, below. The compound class fraction of index for each sample is shown in Figure 7, as well as individually in Figures A22-A40 and Table A2 in Appendix A. Figures 6 and 7 illustrate large primary polysaccharide and phenol fractions in the index of these soil samples.

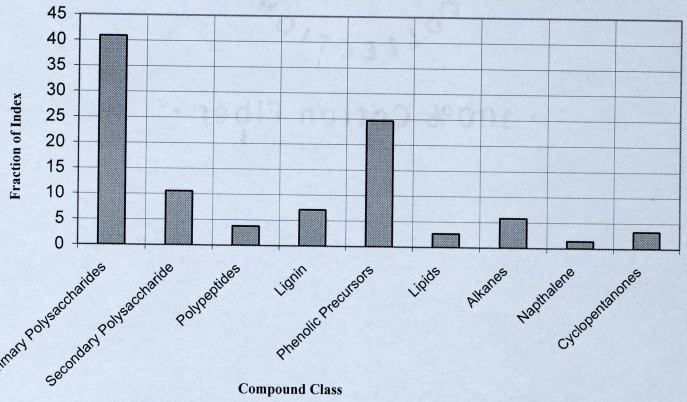


Figure 6: Average SOM compound class fraction of index for incubation soil samples.

Using the data collected from gas chromatography of the incubation headspace, the percentage of CH_4 and CO_2 was found (see Figure 8). Other gases produced by the incubation, such as hydrogen sulfide, were assumed to be minor compared to CH_4 and CO_2. The CH_4/CO_2 ratio was approximately 40:60. The fraction of CH_4/CO_2 gradually increased throughout the incubations.

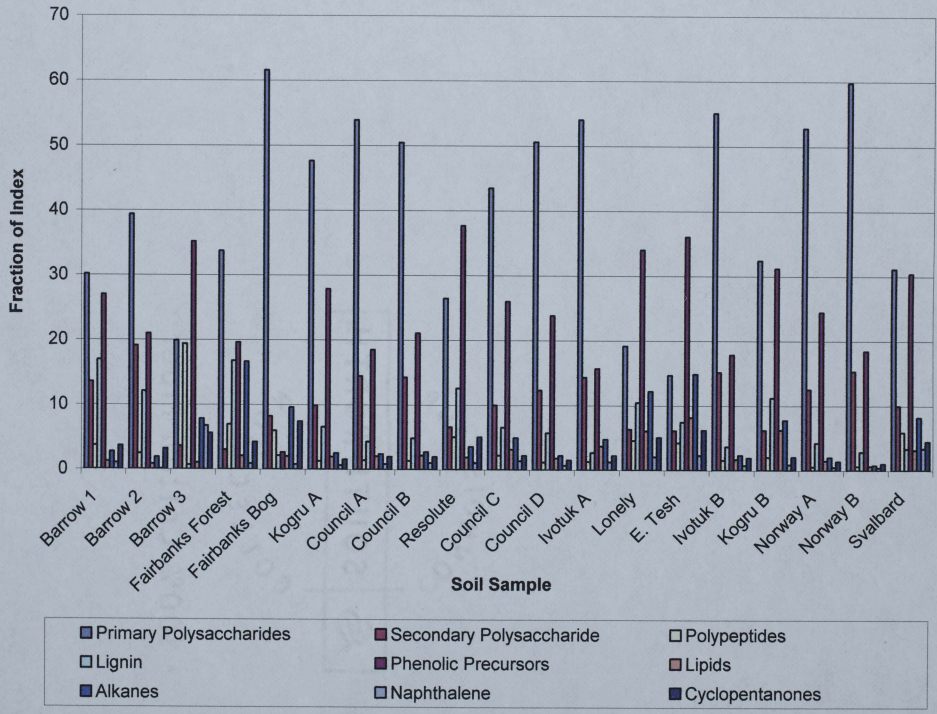


Figure 7: SOM compound class fraction of index for each compound class and incubation soil used.

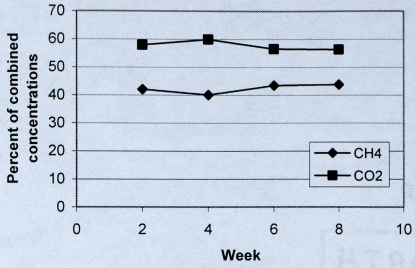


Figure 8: The percent of CH_4 and CO_2 of total gas in the incubations over the course of the incubation period.

The relative amount of CH_4 and CO_2 present in the incubation vessels was calculated using the gas percentages found by gas chromatography and the pressure data (Figure 9). The amount of both gasses increased throughout the incubation. When the CH_4 and CO_2 concentrations were correlated, the value varied from 0.35 to 0.56 throughout the incubation (see Figure 10).

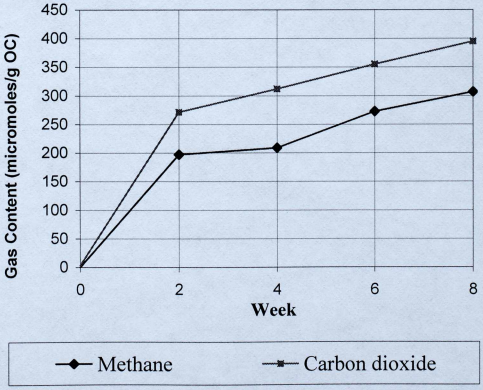


Figure 9: Average amount of CH_4 and CO_2 present in the incubations over the course of the incubation period.

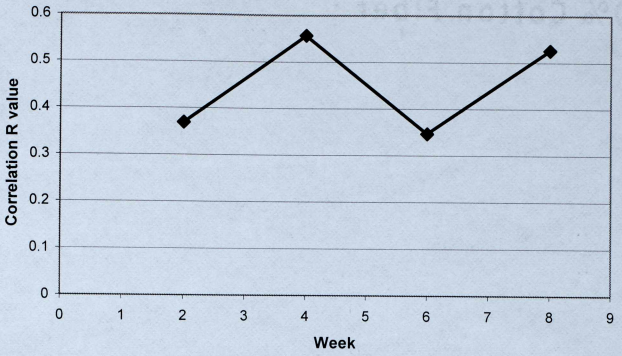


Figure 10: The correlations between CH_4 and CO_2 gas chromatography concentrations in the incubations over the course of the incubation period.

Fifteen of the soils incubated in this experiment were used in aerobic incubations in a study performed by White et al. (2002). The ratio of aerobic gas production to anaerobic gas production from these fifteen soil samples was found (see Figure 10). Figure 11 shows that this ratio varied throughout the incubation period. The correlation between aerobic and anaerobic gas production was high initially ($R = 0.90$), and decreased throughout the incubation (see Figure 12).

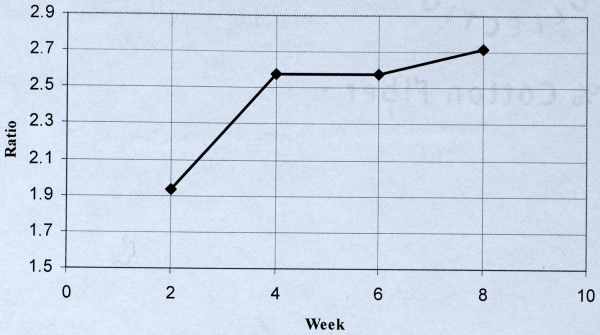


Figure 11: Ratio of aerobic to anaerobic gas production from soil samples. The ratio was performed between the samples used both in this study and a study conducted by White et al. (2002).

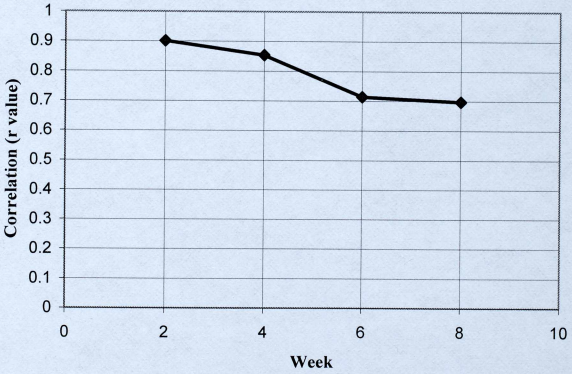


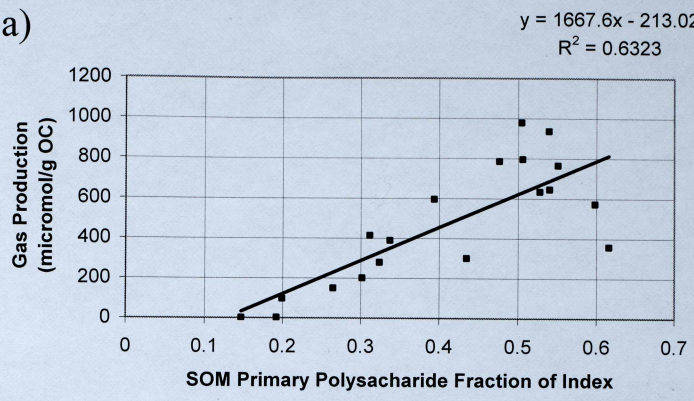
Figure 12: Correlation between gas production under aerobic and anaerobic conditions. Aerobic incubations conducted by White et al. (2002).

Model Development

The pressures for each set of measurements were correlated to the SOM compound class "fractions of index". These correlations were graphed, as shown in Figure 13. Figure 13 shows a graph of the incubation pressure versus primary and secondary polysaccharide content. A best-fit line was drawn through the points on these graphs, resulting in a line relating polysaccharide content and gas production, and an R^2 correlation coefficient. The equation of the best-fit line relating primary polysaccharide content to gas production was used as the model in this study. The R^2 values for the lines relating primary and secondary polysaccharide fractions of index to gas production at the second week of incubation were 0.63 and 0.47, respectively. The equation of the line relating the primary polysaccharide index to gas produced by the second week of incubation was $y = 1667.6 x - 231.02$. This line was used as the model to predict anaerobic respiration potential.

The correlation relating anaerobic gas production to the primary polysaccharide fraction of index was chosen as the model because it had a higher correlation coefficient (R value) than the other correlation values. A higher correlation coefficient indicates a stronger relationship. The correlations resulting from the second week of incubation were chosen for the model because the first measurement value was thought to provide the most realistic model due to the fact that the incubations were closed systems, and closed systems are not present in nature. Additionally, since the changing pressure measurements were being correlated to the initial SOM quality present at the beginning of the incubation, it was thought that the most reliable correlation would be present at the first measurement point.

a)



b)

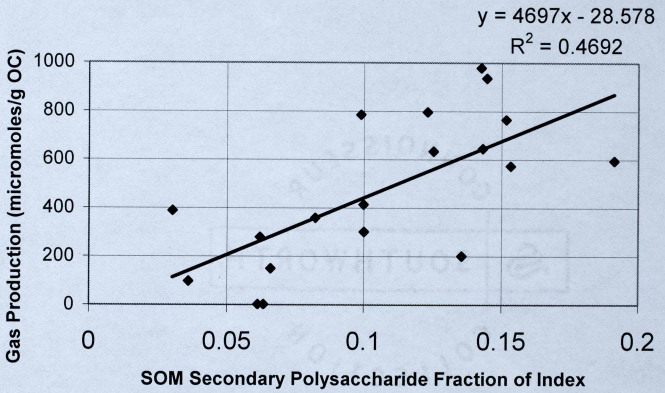


Figure 13: Graphs showing incubation gas pressure and polysaccharide content. Gas pressure is the pressure on the second week of incubation. X axis is a) SOM primary polysaccharide content and b) SOM secondary polysaccharide content.

The correlation between the incubation pressure and all the SOM compound class fractions of index, as well as soil organic matter content, are shown in Figure 14. Figure 14 shows that the primary and secondary polysaccharide fractions of index were more positively correlated to anaerobic gas production potential than the other indices. Initially, the primary polysaccharide fraction of index showed a higher correlation than

the secondary polysaccharide fraction of index. A trend of a decreasing correlation for the primary polysaccharide index with time, and an increasing correlation with secondary polysaccharides with time, caused the secondary polysaccharide index to exhibit higher correlation values than the primary polysaccharide index in the sixth and eighth weeks of incubation. The correlation between incubation pressure and the primary polysaccharide fraction in index was higher than the correlation between incubation pressure and organic matter content during weeks 2, 4, and 6 of the incubation. The correlation between incubation pressure and the secondary polysaccharide fraction of index was higher than the correlation between incubation pressure and organic matter content at all measurement points.

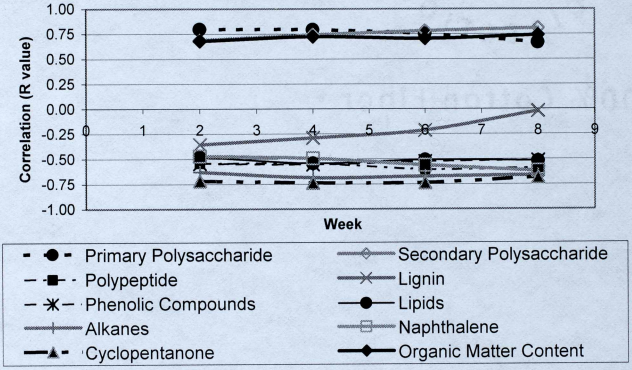


Figure 14: Time dependent correlations between cumulative incubation pressure, and SOM indices and organic matter content.

Model Application

Soil cores were taken from tussock, trough, and low-density black spruce forest vegetation types during the summer of 2003. Soil cores were taken from medium density black spruce forest and dense black spruce and aspen forest during the summer of 2004. The depths of these soil cores are shown in Figure 15. Since the samples were taken to the depth of the permafrost, the depth of the core increased throughout the summer until the point that the surface of the ground froze, preventing additional sampling.

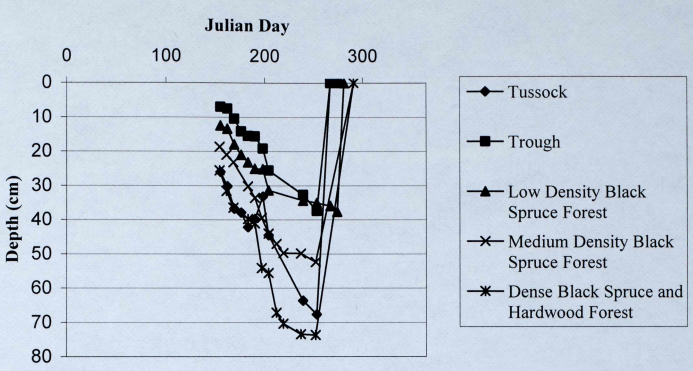


Figure 15: Graph of the depth of soil cores taken near the Smith Lake Methane Flux Site

The SOM content by weight of the soil samples taken are shown in Figure 16. The average SOM content of the soil sections generally decreased with increasing depth in all vegetation areas. The organic matter content also decreased with increasing forest density. The O horizon of tussock, trough, and low-density forest samples had very high percentages of organic matter.

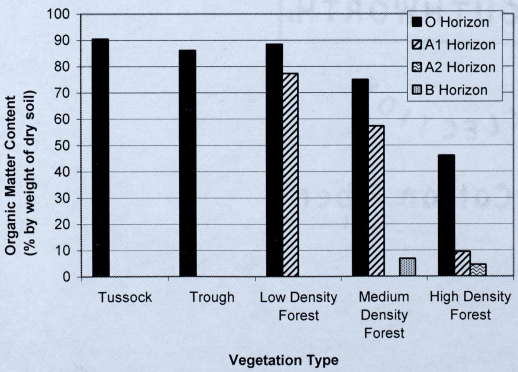


Figure 16: Organic matter content of the horizons of the 5 vegetation types studied.

The relative abundances of the primary and secondary polysaccharide indices in the O and A horizons of the five vegetation areas sampled are shown in Figure 17. These graphs show that there is more variability in the primary polysaccharide index than the secondary polysaccharide index in both the O and A horizons of all vegetation areas.

The model was used to predict the anaerobic gas production from the SOM polysaccharide fraction of index in the soil cores shown in Figure 15. The results were matched to the color scheme shown in Figure 18. Using this color scheme, blue tones represent lower respiration potential while red tones represent high respiration potential. Frozen soil was represented by white. Soil for which data were not available was shown in gray.

The results of the model application, using the color scheme shown in Figure 18, are shown in Figures 19-23. Figure 19 shows that the primary polysaccharide fraction of index and predicted anaerobic gas production potential in the tussock vegetation area was high in the middle of the summer and low at the end of the summer.

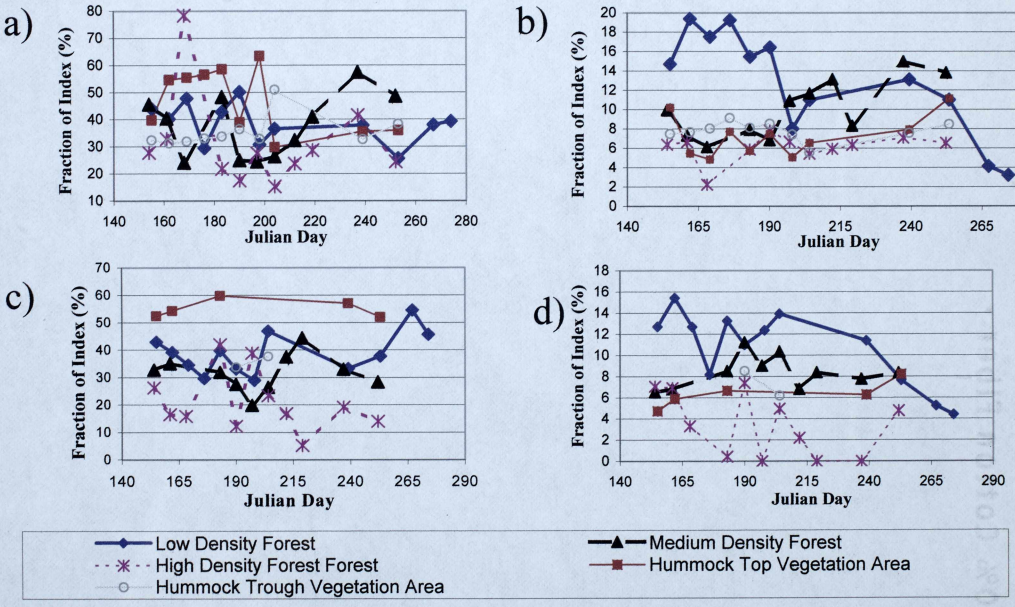


Figure 17: The fraction of index of primary and secondary polysaccharides of the five vegetation areas sampled. a) Primary polysaccharide index abundance of the O- horizon of soil core samples. b) Secondary polysaccharide index abundance of the O-horizon of soil core samples. c) Primary polysaccharide index abundance of the A- horizon of soil core samples. b) Secondary polysaccharide index abundance of the A-horizon of soil core samples.

Anaerobic Gas Production Potential		
Color Code	µmoles gas/ (g^{-1} organic C * two weeks of incubation)	Relative magnitude of gas production
	<100	LOW
	100-199	
	200-299	
	300-399	MEDIUM
	400-499	
	500-599	
	600-699	
	700-799	HIGH
	800-899	
	>900	
	frozen soil	
	no data	

Figure 18: Color scheme used to show predicted values of respiration.

Figure 20 shows that the primary polysaccharide fraction of index and predicted anaerobic gas production potential in the trough vegetation area was relatively constant throughout the summer. Figure 21 shows that the primary polysaccharide fraction of index and predicted anaerobic gas production potential in low-density forest varied throughout the summer. Figure 22 shows that the primary polysaccharide fraction of index and predicted anaerobic gas production potential in medium-density forest was generally lower in midsummer than in early or late summer. Figure 23 shows that the primary polysaccharide fraction of index and predicted anaerobic gas production potential in high-density forest was generally low throughout the summer, although a few

soil sections showed high primary polysaccharide contents and thus predicted high anaerobic gas production potential.

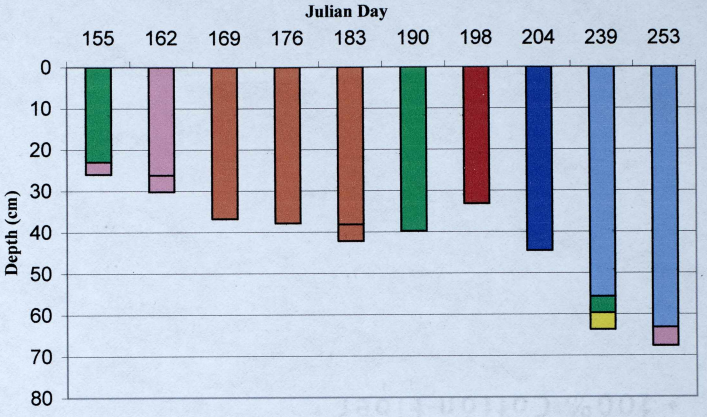


Figure 19: Predicted anaerobic respiration potential in Tussock soil cores.

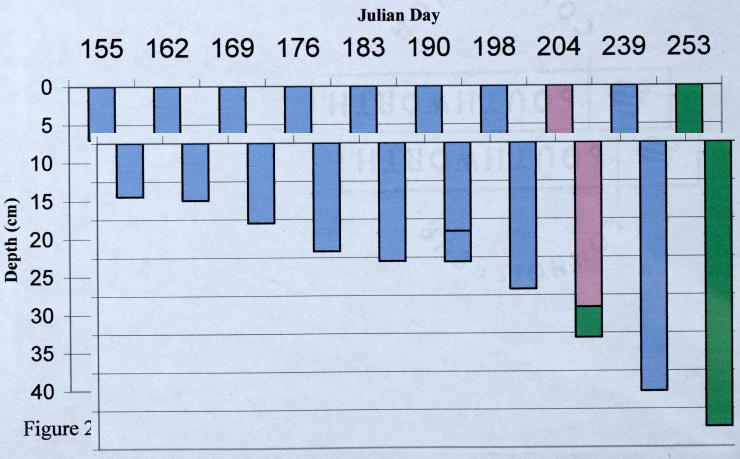


Figure 2

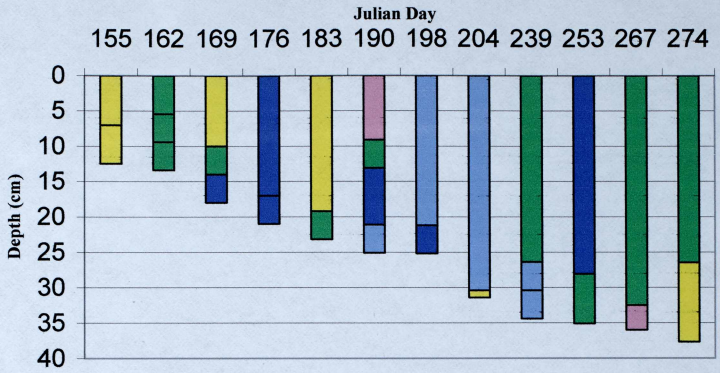


Figure 21: Predicted anaerobic respiration potentials in low density black spruce forest soil cores.

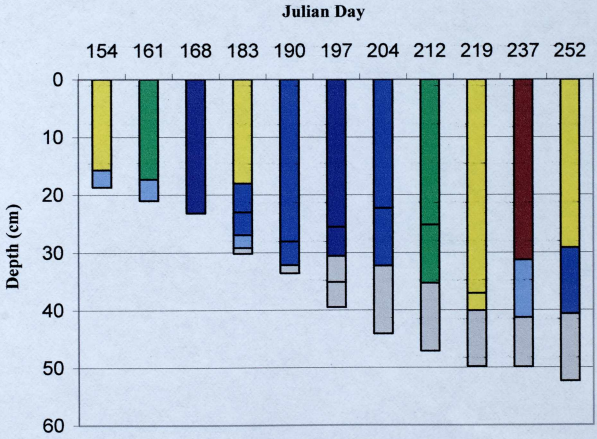


Figure 22: Predicted anaerobic respiration potentials in medium density black spruce forest soil cores.

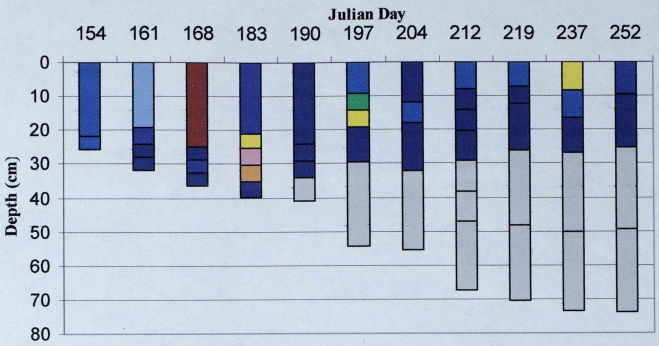


Figure 23: Predicted anaerobic gas production in dense black spruce hardwood forest soil cores.

Maps of the predicted anaerobic gas production near the Smith Lake Methane Flux Site were constructed from a 2003 photograph of the area, taken with a pixel resolution of 1 meter. The maps were constructed by dividing up a photograph of the area into areas of tussocks and troughs, and low, medium, and high density forest. Figure 24 shows a map of the distribution of these vegetation areas.

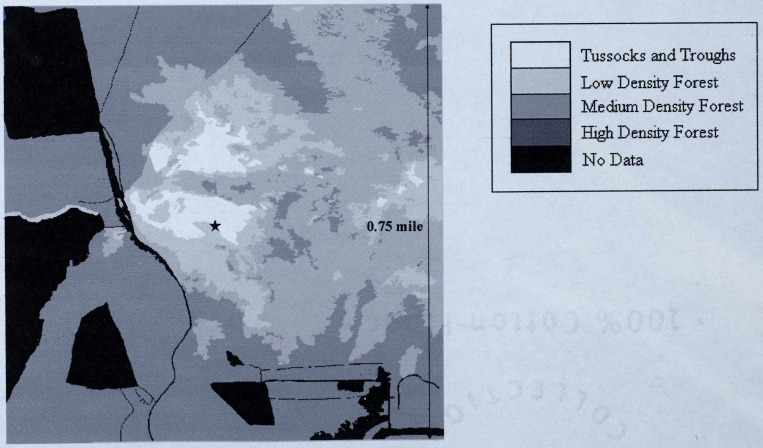
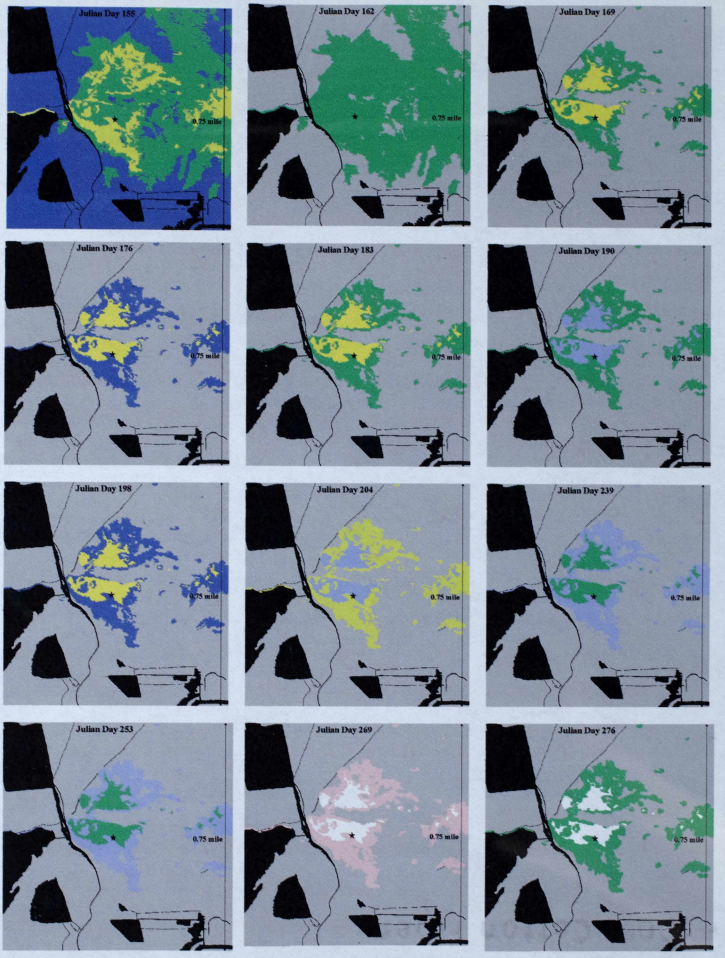


Figure 24: Distribution of vegetation areas around Smith Lake Methane Flux Site (indicated by star in center of map).

Three series of maps were constructed of the predicted anaerobic gas production potential in the different vegetation areas within 0.75 miles of the Smith Lake Methane Flux Site. The predictions in Figure 25 were derived from soil cores taken during the summers of 2003 and 2004. The predictions in Figure 26 were derived from soil cores taken during the summer of 2003. The predictions in Figure 27 were derived from soil cores taken during the summer of 2004. The maps show the change in estimated anaerobic gas production potential over the course of the summer season. The predicted amount of anaerobic gas production potential in these areas was found using the predictions shown in Figures 19-23. The same color scheme (shown in Figure 18) was used in the Figures 19-23 and Figures 25-27. Since the maps were made based on soil cores taken from two field seasons, three maps were constructed in order to provide a map of anaerobic respiration potentials based on each field season, and a combination of both field seasons. Figures 25 and 27 only show the estimated anaerobic gas production during Julian days 154 and 161 for field season 2004.

The cumulative predicted anaerobic gas production over the course of a summer season was found (see Figure 28). This calculation is shown in Appendix C. Per square meter of land area, medium density spruce forest was found to have the largest cumulative gas production, followed by low-density forest, tussocks, high-density forest, and troughs.

The relationship between SOM primary polysaccharide fraction of index and moisture content in the low, medium, and high-density forest vegetation soil samples was investigated by correlating these two variables (see Figure 29). The highest correlation found had an R^2 correlation value of 0.21. There was no significant correlation between moisture content and primary polysaccharide fraction of index in these sampling areas.


Julian Day 155
0.75 mile
Julian Day 162
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Julian Day 276
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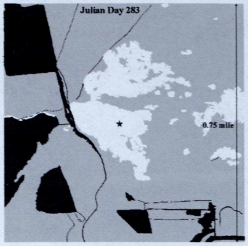
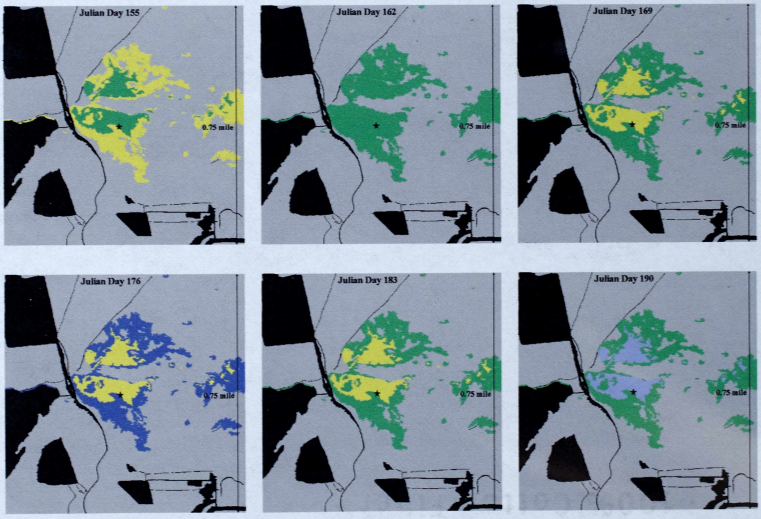


Figure 25: Map 1: Predicted anaerobic gas production potential in areas surrounding the Smith Lake Methane Flux Site (shown by a star in center of map). Predictions are based on soil cores taken during the summers of 2003 and 2004. Refer to Figure 18 for the color scheme used.



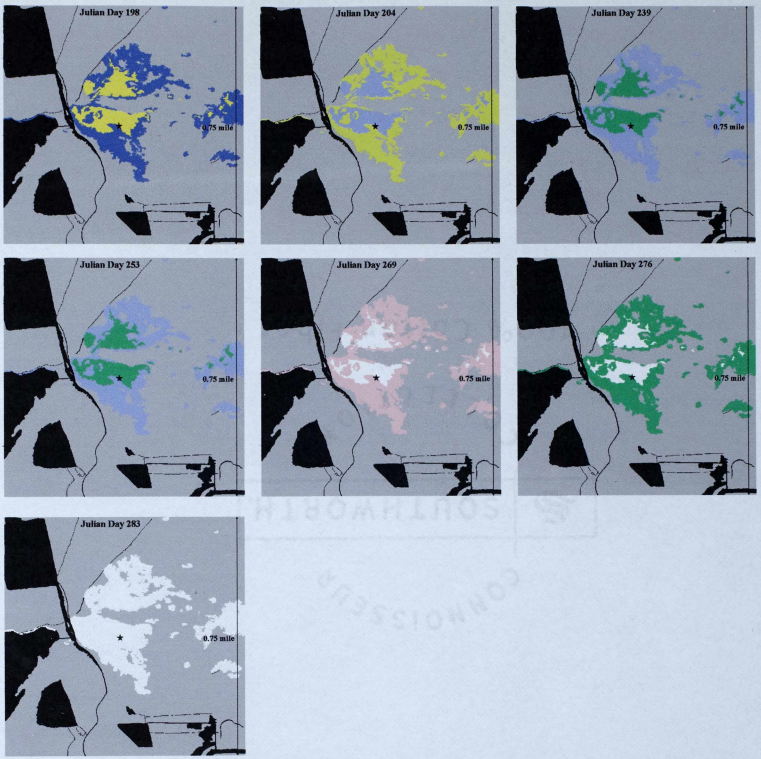


Figure 49: Map 2: Predicted anaerobic gas production potential in areas surrounding the Smith Lake Methane Flux Site (shown by a star in center of map). Predictions are based on soil cores taken during the summers of 2003. Refer to Figure 18 for the color scheme used.

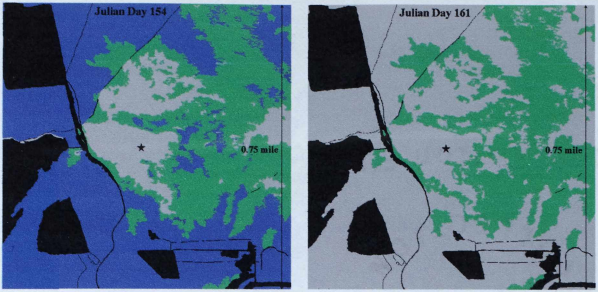


Figure 27: Map 3: Predicted anaerobic gas production potential in areas surrounding the Smith Lake Methane Flux Site (shown by a star in center of map). Predictions based on soil cores taken during the summers of 2004. Refer to Figure 18 for the color scheme used.

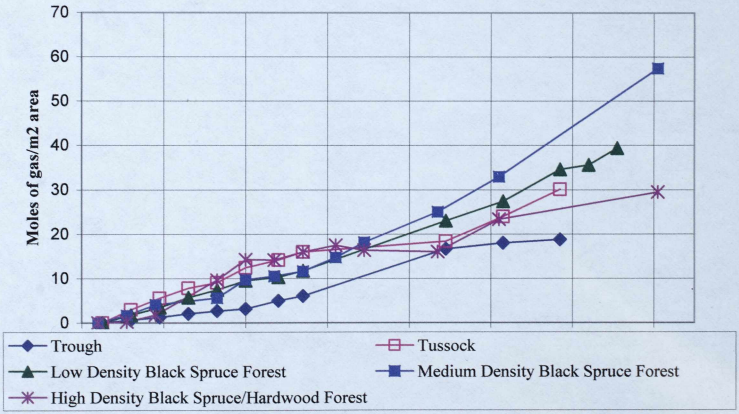


Figure 28: Cumulative summer anaerobic gas production per square meter of land in different vegetation areas.

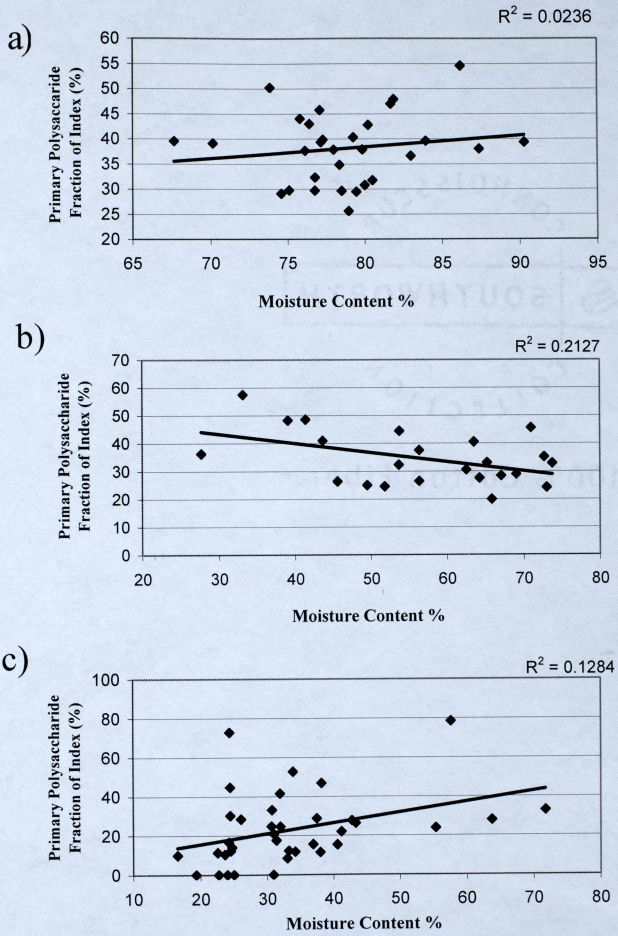


Figure 29: Graphs relating SOM primary polysaccharide content to moisture content. X axis is the moisture content in a) low density spruce forest, b) medium density spruce forest, and c) high density spruce and hardwood forest.

Error Analysis

Six replicate incubations of soil from Council, Alaska (Council C) were performed in order to quantify experimental error. The 95% confidence interval for the pressure during the second week of incubation was 0.44 psi. The 95% confidence interval in the pressure during the fourth week of incubation was 0.37 psi (see Figures 30 and 31).

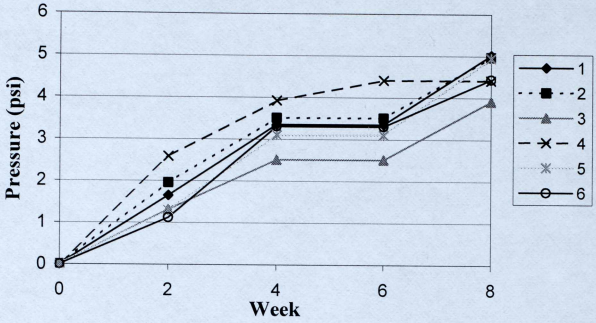


Figure 30: Graph showing the variation in pressures resulting from replicate incubations. Alternative minimum pressures are used.

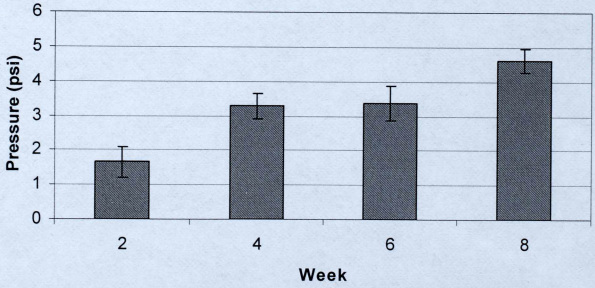


Figure 31: Average pressure and 95% confidence intervals from replication incubations. Alternative minimum pressure values are utilized.

Five replicate soil cores were taken in the low-density forest vegetation area. The polysaccharide fractions of index in these soil cores are shown in Figure 32 below. Figure 32 shows that there is variability in the polysaccharide fractions of index of these samples.

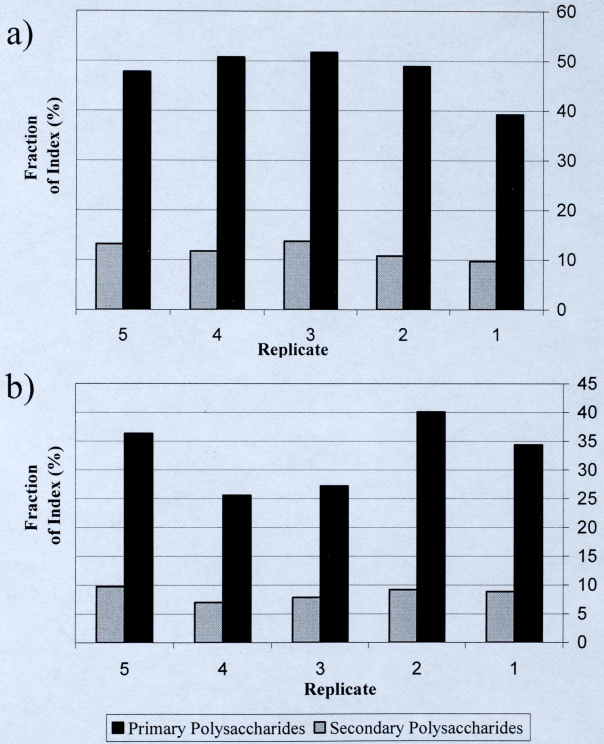


Figure 32: Polysaccharide fraction of index in replicate soil core sections. a) O-horizon replicate soil core sections. b) A-horizon replicate soil core sections.

Application of the model using the color scheme shown in Figure 18 to the replicate soil cores shows that anaerobic gas production varied in both the O and A horizons (see Figure 33). The 95% confidence interval for the O horizon was 72 μmoles per g organic carbon per two weeks, and 90 μmoles per gram organic carbon per two weeks for the A horizon. The division between color in this color scheme is 100 μmoles per gram organic carbon per two weeks. This indicates that soil heterogeneity accounts for variations in estimated anaerobic gas production using this model, and this variation is shown in the color scheme by uncertainty between adjacent colors.

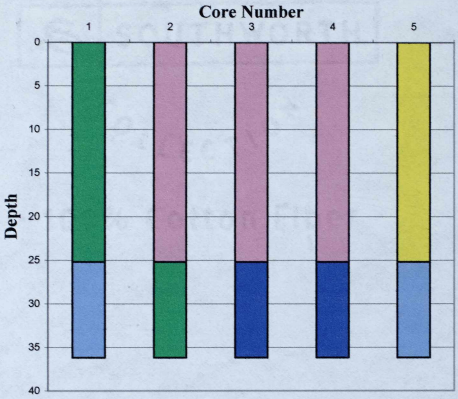


Figure 33: Estimated anaerobic gas production potential in 5 replicate low-density forest soil cores. Utilized color scheme shown in Figure 18.

Discussion

Laboratory Experiments

A number of other studies have been conducted that measured CH_4 production in anaerobic incubations (see Table 2). Rates of CH_4 production in all other studies were lower than in this study. Moore and Dalva (1997), Yavitt et al. (1988), and Brown et al. (1989) performed incubations that produced the same order of magnitude of CH_4 as this study. When comparing values of CH_4 production in soil incubations, it is important to note that different studies used different incubation methods. Magnusson (1993) excluded anaerobic gas production during the first 4 days of incubation when calculating gas production rates. Williams and Crawford (1984) conducted incubations at the native pH of the soils. The arctic pH may have resulted in a significantly lower potential rate of methanogenesis. In this study the native pH of most of the soils was about 4.5 (see Table A-1), and the soils were all neutralized in order to eliminate differences in gas production due to pH differences.

The correlation between CH_4 and CO_2 abundance was found to vary between 0.35 and 0.56 (see Figure 10). Moore and Dalva (1997) similarly found the average CH_4:CO_2 correlation to be 0.36.

An initial ratio of aerobic to anaerobic gas production of about 1.9 was found (see Figure 11). The ratio increased throughout the incubation to a ratio of about 2.7 by the eighth week of incubation. Moore and Dalva (1997) similarly found a 2:1 ratio of aerobic to anaerobic CO_2 production. The correlation between aerobic and anaerobic gas production was found to decrease from about 0.9 initially, to about 0.7 by the eighth week of incubation (see Figure 12). Moore and Dalva (1997) found that aerobic and anaerobic CO_2 production were correlated with an R value of 0.581.

Table 2: Comparison of methane emission measurements from incubations in this and other studies.

Study	Site Description	μgrams CH_4/drysoil/hr	Comments
This Study	Barrow 1, AK	3.28	conducted at pH 7, 20°C, average of 14 days of incubation, vessel degassed with N_2, vessels shaken continuously
	Barrow 2, AK	11.06	
	Barrow 3, AK	0.07	
	Fairbanks, AK spruce forest	7.06	
	Fairbanks, AK bog	6.27	
	Kogru A, AK	14.76	
	Council A, AK	17.22	
	Council B, AK	18.21	
	Resolute, Canada	2.15	
	Council C, AK	5.17	
	Council D, AK	14.97	
	Ivotuk A, AK	10.97	
	Lonely, AK	0.00	
	Teshekpuk Lake, Alaska	0.00	
	Ivotuk B, AK	12.85	
	Kogru B, AK	4.18	
	Saltfjall, Norway	12.42	
	E. of Mo I Rana, Norway	10.99	
	Svalbard, Norway	0.74	
Moore and Dalva (1997)	peatland and wetlands, Canada	0.13	continuously shaken, degassed with N_2, 5 days incubated, 20°C
Magnusson (1993)	northern Sweden	0.27	16°C
Moore and Knowles (1990)	subarctic fen, Canada	0.00 – 4.17	15°C, 12 day incubation
Brown et al. (1989)	bog, Ottawa, Canada, surface peat	0.01 - 1.00	average of 1 week of incubation, 25°C, vessel degassed with CO2 and H_2
	bog, Ottawa, Canada, subsurface peat	0.01 - 0.08	
Yavitt and Lang (1988)	Appalachian Mtns., West Viginia	0.22 - 5.56	19°C, no shaking of incubation vessel, 9 day incubation period
Williams and Crawford (1984)	Minnesota, USA surface peat	0.22	conducted at native pH, average of 100 hours of incubation, 25°C
	Minnesota, USA 15cm depth	0.21	
	Minnesota, USA 40 cm depth	0.2	

Model Development

The results of this study successfully showed that an SOM quality index could be correlated to anaerobic gas production. Primary and secondary polysaccharide indices were found to be positively correlated to anaerobic gas production potential, while the other compound classes analyzed were negatively correlated to anaerobic gas production potential (see Figure 14). The negative correlation between some compound classes and anaerobic gas production probably does not indicate inhibition of microbial respiration by these compounds. Instead, when large quantities of compounds with negative correlation were present large quantities of polysaccharides were not. Updegraff et al. (1995), in a study that correlated the results of anaerobic incubations to broad soil organic matter elements, similarly found C mineralization to be positively correlated to the fraction of small labile elements and methanogenesis to be negatively correlated with the fraction of recalcitrant compounds. In this study primary and secondary polysaccharides were relatively labile, while the others compound classes were recalcitrant in comparison. It is likely that most gas production was caused by polysaccharide degradation.

The correlation coefficient between anaerobic gas production and the polysaccharide fractions of index were as high as 0.80 (r^2 = 0.64) for primary polysaccharides, and 0.81 (r^2 = 0.65) for secondary polysaccharides (see Figure 14). The primary polysaccharide correlation was found to decrease throughout the incubation. The most probable explanation for this decrease in correlation was the preferential use of primary polysaccharides as substrates by the microorganisms present. Since the correlations were performed with the soil organic matter quality at the beginning of the incubation, the correlation between anaerobic gas production and primary polysaccharide fraction of index decreased throughout the incubation as the primary polysaccharide content of the incubations decreased. As primary polysaccharides were consumed, more secondary polysaccharides were used as substrates, causing the correlation between secondary polysaccharides and anaerobic gas production to increase.

The correlation between organic matter content and anaerobic gas production was generally lower than the correlation between polysaccharide fraction of index and

anaerobic gas production. White et al. (2000) used the same SOM index used in this experiment to correlate aerobic incubation gas production to SOM quality, and similarly found that the index was more correlated to microbial gas production than the correlation between organic matter content and microbial gas production.

The correlation between the primary polysaccharide index and gas production during the second week of incubation was chosen as the point with which to predict anaerobic gas production for other soils. This first measurement point was chosen because an extended incubation causes the unnatural conditions of an isolated system to be exaggerated. The first measurement was taken after two weeks of incubation in order to ensure that the pressures present were large enough to be recorded by the experimental apparatus used. The correlation with the primary polysaccharide fraction of index was also chosen because primary polysaccharides composed the highest fraction of index, and exhibited the highest correlation. Strongly positively correlated compounds were examined as potential components of the model instead of strongly negatively correlated compounds because it is better to base the model on a compound that influences anaerobic gas production than on a compound whose presence decreases anaerobic gas production.

Model Application

Application of the model would predict higher anaerobic gas production from soils with a high content of polysaccharides in the organic matter. Soils that contain high percentages of organic matter by weight would also presumably also have a high bulk content of polysaccharides, relative to soils that contain a low percentage of organic matter. Based on this, high anaerobic gas production can be related to soils with high organic matter contents, and high contents of primary polysaccharides. Magnusson's (1993) results were in agreement with this statement by finding that anaerobic incubation of topsoils produced more CH_4 than moderately humified peat, which produced more CH_4 than well humified peat.

The linear model resulting from the correlation between anaerobic gas production and the primary polysaccharide index allowed for the construction of graphs and maps of predicted anaerobic gas production in the area surrounding the Smith Lake Methane Flux Site at the University of Alaska, Fairbanks. When evaluating these graphs it is important to understand that these predictions are for the ideal anaerobic conditions used in model development in the laboratory, which isolates the differences in SOM quality. Other factors, such as the effect of pH and temperature, were not considered. The developed models were applied to five different vegetation types at the Smith Lake Methane Flux Site. The type of surface vegetation present is important in this study because soils with different decomposing plant life will create a soil that contains different organic matter (Wilson et al., 1983).

Graphs of the predicted anaerobic gas production potential over the summer of 2003 in tussock soil cores showed an increase in anaerobic gas production potential in the beginning of the summer and a decrease in anaerobic gas production potential at the end of the summer season (see Figure 19). The divisions between early, middle, and end of summer in the tussock vegetation area are roughly Julian days 165 and 200. This result suggests that anaerobic gas production potential was highest in mid summer and lowest in late summer. The decrease in polysaccharide content at the end of the summer may have been due to a decomposition of all easily degradable substrates.

Trough soil cores showed a relatively constant level of anaerobic gas production potential throughout the summer (see Figure 20). This result suggests that SOM quality in the trough vegetation area was relatively low and constant throughout the course of the summer. Although our model would predict higher CH_4 production in tussocks than troughs, based solely on the primary polysaccharide index, this isn't necessarily the result to be expected in the field because troughs are more likely to be anaerobic than tussocks. Moore and Knowles (1990) studied CH_4 emissions in a patterned subarctic fen where the height of the water table varied within the fen. The CH_4 emission in the fen was found to increase as the height of the water table increased. Bubier et al. (1993) found that hollows produced a 5-60 times larger CH_4 flux than hummocks in wetlands in northern Ontario,

Canada. Field results such as these are highly dependent on natural conditions at the time of sampling. Bubier et al (1993) results may be a reflection of the soil moisture. If all the soil were inundated with water, the results may have been different. Our model is based on ideal anaerobic conditions that isolate the single variable of SOM quality, which may produce CH_4 flux estimates that deviate from what would be produced *in-situ*. Sites with high SOM quality may not possess some other attributes such as nutrient availability for biological decomposition. While tussocks may have higher SOM quality, conditions in the troughs or hollows are more conducive to decomposition. This stands to reason since sites with high flux rates would have rapid decomposition of substrates, resulting in depressed SOM quality. Whalen and Reeburgh (1992) concluded that the relationship between CH_4 and any single variable are site specific and are of little value as flux predictors; an integrating predictor is needed for accurate CH_4 emission prediction.

The model predicted variations in anaerobic gas production potential in low-density black spruce forest soil cores over the course of the 2003 summer season (see Figure 21). This was a result of variations in SOM quality over the course of the summer. Variability in *in-situ* CH_4 emissions has been found by a number of studies. Moore and Knowles (1990) found that coefficients of variation of methane emission measurements were about 100%, and at the subarctic sites studied, 85% of the variability was associated with the spatial variability between measurement locations. Whalen and Reeburgh (1992) found that coefficients of variation for CH_4 emission ranged between 67 and 118% at different sample sites in Alaskan arctic tundra. Lessard et al. (1994) found that up to 452 field measurements may be necessary to obtain a gas flux measurement with 10% accuracy.

In medium density forest soil cores the model predicted a trend of low anaerobic gas production potential roughly between Julian days 168 and 212, with higher production potential in the early and late summer season (see Figure 22). In high density forest soil cores the model predicted generally low anaerobic gas production potential throughout the summer, although some sections showed higher gas production potentials (see Figure 23). The different seasonal trends in anaerobic gas production potential in the

different vegetation areas may be due to different rates of freezing and thawing of the soil, different moisture and temperature regimes, and different vegetation cover.

The predictions for all of the vegetation areas sampled were also displayed on maps of the Smith Lake Methane Flux Site that were divided up by vegetation type (Figures 24-26).

It is interesting to note that in some of the cores sampled, the polysaccharide fraction of index increased with increasing depth. This may have been due to mixing of the soil horizons during cryoturbation. Cryoturbation of less decomposed material to deeper soil horizons is common in arctic and subarctic soils. Using the developed model, a larger volume of gas per gram of organic carbon was predicted from lower soil horizons in these cores. In the field, this result would be countered by a number of factors, most notably the fact that lower soil horizons are colder than upper soil horizons during most of the thawed period. Hobbie et al. (2000) found that most lower soil horizons have slower decomposition rates than fresh litter due to the accumulation of recalcitrant compounds and to cold temperatures. However, Moore and Knowles (1990) found that, although generally there was a decrease in methane production with depth, a few of the samples studied showed higher CH_4 production in lower horizons. Williams and Crawford (1984) also found that CH_4 production in Minnesota peat generally decreased with increasing depth, but some deeper soil sections were found to produce more CH_4 than overlying soil layers.

Although this study only focused on the change in relative polysaccharide content between samples, other studies examined the change in other SOM compounds. Schulten (1993) found that an A horizon soil yielded large quantities of phenol derivatives, while a B horizon soil yielded large quantities of alkanes and olefins. This fact suggests further research opportunities with the present data set.

The five vegetation areas sampled showed differences in maximum depth of thaw. Tussock, trough, and low-density black spruce forest, all sampled during the summer season of 2003, showed depths of thaw of 67.7cm, 37.4cm, and 37.7cm, respectively. Medium and high-density spruce forest, sampled during the summer season of 2004,

showed depths of thaw of 52.4cm, and 73.7cm, respectively. Whalen and Reeburgh (1992) found that the depth of thaw at various sites at the University of Alaska Arboretum ranged between 55 and 85cm during the summer seasons from 1987 to 1990. Whalen and Reeburgh (1992) concluded that an increase in thaw depth of permafrost will not have a large stimulatory effect on methanogenesis because deeper peat is likely to be refractory. This study supports Whalen and Reeburgh's hypothesis by characterizing the SOM quality of lower soil horizons. The lower soil horizons in medium and high forest soil cores had a relatively low concentration of organic matter content (<7% by weight). However Vourlitis et al. (1993) found that CH_4 emission near Prudhoe Bay, Alaska was strongly controlled by thaw depth, and concluded that this ecosystem would have a strong response to global climate change.

Analysis of the cumulative amount of anaerobic gas production potential in the five vegetation areas sampled (see Figure 28) provides a more realistic perspective of the actual amount of gas production because the density of organic matter is taken into account. This graph shows that, given ideal anaerobic conditions, medium density forest would produce the most gas. The results shown in Figure 28 are affected by the differences in rates of thaw throughout the summer, and refreezing rates at the beginning of winter. Figure 28 is an underestimate of the true predicted value because the bottom of the soil cores taken in the latter part of the summer was ignored due to low SOM content.

As listed in Table 3 below, other studies have been conducted that estimate CH_4 production per square meter of land area. Yavitt et al. (1988) similarly made estimates of CH_4 emission based on incubation results, and produced results that were similar to the rates estimated by this experiment. Moore and Knowles (1990) and West et al. (1999) estimated CH_4 emission based in-situ measurements of production, and found actual emissions to be much lower than the emission under ideal laboratory conditions found by Yavitt and Lang (1988) and this study.

This study found that the primary polysaccharide index was not correlated to moisture content in the sampling areas used (Figure 29). Moisture content can play a role in organic matter content on a short time scale by the leaching of labile organic

compounds during high rainfall events (Wilson et al., 1983). However, precipitation initiated leaching of organic compounds did not appear to be present in this soil during the sampling period used in this study.

Table 3: Comparison of methane emission measurements between this and other studies.

Table 3: CH_4 emission prediction compared to other studies.			
Study	**Site Descriptions**	**g CH_4/m^2day**	**Comments**
This Study	Tussock	1.35	Based on incubation results
	Trough	0.73	
	Low Density Spruce Forest	0.97	
	Medium Density Spruce Forest	1.04	
	Dense Spruce/Hardwood Forest	0.57	
Mer and Roger (2001)	upland soils temporarily submerged	0 - 0.02	
	freshwater environment without plants	0 - 1	
	peatlands	0 - 0.2	
West et al. (1999)	*Carex* dominated alpine tundra	0 - 0.03	Based on in situ measurements
Moore and Knowles (1990)	subarctic poor fen, Canada	0.03 - 0.05	Based on in situ measurements
	subarctic patterned fen, Canada	0.02 - 0.2	
	subarctic peatlands, Canada	0.01 - 0.3	
Yavitt and Lang (1988)	Appalachian Mtns., West Viginia	0.19 - 0.77	Based on incubation results

When applying these results to the natural environment, it should be understood that this is only a model to isolate the influence of SOM quality. It is important to consider the fact that this study represents the maximum of expected values for methane flux in the field, since this study was carried out under ideal anaerobic conditions. The pH was neutralized, all oxygen was removed from the headspace of the bottles before the incubation was conducted, the samples were submerged in water and shaken, the incubations were conducted at room temperature, and nutrients were added prior to beginning the incubation. The only variable not altered that may affect microbial activity was salinity. Many soils in the Arctic and sub-Arctic have low pH values (Yavitt et al., 2004; Bubier et al., 1993) and experience cold temperatures even when thawed. These factors alone may drastically affect anaerobic gas production. Additionally, many

northern soils have poor nutrient quality (Rask et al., 1992), and may experience mass transfer limitations that prevent good nutrient and substrate distribution. Another factor present in natural systems is the presence of methanotrophs in aerobic soils located above methanogenic anaerobic soils. Methanotrophs in upper soil horizons can consume CH_4 before it can be released into the atmosphere, and may oxidize up to 90% of CH_4 produced in anoxic soils before it can be released into the atmosphere (Mer and Roger, 2001; Yavitt et al., 1988). It is also thought that there may be methanotrophs that can survive on substrates other than CH_4 in anoxic soils (Moore and Dalva, 1997). The amount of CH_4 released to the atmosphere in natural systems is also dependent on the transport mechanism between the soil and atmosphere. Common transport mechanisms are diffusion, ebullition, and plant-mediated transport (Mer and Roger, 2001; Moore and Dalva, 1997).

Error Analysis

Six replicate incubations of a soil from Council, Alaska showed there was a relatively large experimental error in the method of conducting incubations (see Figures 30 and 31). The 95% confidence interval, 0.44 psi, is 27.5% of the average pressure of 1.6 psi, after two weeks of incubation.

Five replicate soil cores in the low-density forest vegetation area also showed that there is experimental error in the analysis of SOM quality (see Figures 32 and 33). The 95% confidence intervals for both the O and A horizons of the replicate cores were large, (72 and 90 μmoles gas/g OC). This represents a large portion of the division between the colors used in the color scheme. This leads to the conclusion that there may often be little difference between the estimated anaerobic gas production in soil sections that are labeled with adjacent colors in this color scheme.

There are a number of sources of experimental error that need to be considered. The problem of clogged needles during pressure measurement was partially remedied by using alternative minimum pressures. However, this method could not predict the actual pressure at that time, and thus was only a partial solution.

Conclusions

In conclusion, this research has produced a number of important results:

- An index of organic compounds could correlated to anaerobic gas production.
- The primary polysaccharide fraction of index was positively correlated to anaerobic gas production ($r^2 = 0.64$).
- Anaerobic gas production was more correlated to the polysaccharide fraction of index than the weight percent of organic matter present in the soils studied.
- The correlation between CH_4 and CO_2 abundance was found to vary between 0.35 and 0.56, with an average correlation of 0.45.
- An initial ratio of aerobic to anaerobic gas production of about 1.9 was found. The ratio increased throughout the incubation to a ratio of about 2.7 by the eighth week of incubation. The correlation between aerobic and anaerobic gas production was found to decrease from about 0.9 initially, to about 0.7 by the eighth week of incubation.
- Application of the model to five areas of differing vegetation cover at the Smith Lake Methane Flux Site produced different results. The tussock vegetation area showed an increase in anaerobic gas production potential in the beginning of the summer and a decrease in anaerobic gas production potential at the end of the summer season. The trough vegetation area showed a relatively constant level of anaerobic gas production potential throughout the summer. Low-density black spruce forest soil cores showed a variation in anaerobic gas production potential over the course of the 2003 summer season. In the medium density forest vegetation area, a trend of low anaerobic gas production potential roughly between Julian days 168 and 212 was found, with higher production potential in the early and late summer season. In the high-density forest vegetation area, there was generally low anaerobic gas production potential throughout the summer, although some sections showed higher gas production potentials.
- In some of the cores sampled, the polysaccharide fraction of index increased with increasing depth. This may be due to cryoturbation of less decomposed material

to deeper soil horizons. Using the developed model, a larger volume of gas per gram of organic carbon was predicted from lower soil horizons in these cores. In the field, this result would be countered by a number of factors, most notably the fact that lower soil horizons are colder than upper soil horizons during most of the thawed period.

- Medium density forest was found to have the highest cumulative amount of anaerobic gas production potential, given ideal anaerobic conditions.
- Tussock, trough, and low-density black spruce forest, all sampled during the summer season of 2003, showed depths of thaw of 67.7cm, 37.4cm, and 37.7cm, respectively. Medium and high-density spruce forest, sampled during the summer season of 2004, showed depths of thaw of 52.4cm, and 73.7cm, respectively.

Future Work

Future work in this subject may include improving the model by the incorporation of soil salinity measurements, increasing the number of soil samples used in incubations, and testing the model. The composition of the soil can be measured after degradation to learn how the degradation changes the SOM quality. A multivariate model including different compounds, and variables, such as temperature and pH, would provide a model that would predict anaerobic gas production under field conditions. A better understanding of the surface vegetation and salinity of the soil samples used in the incubation may also allow for model improvements.

An understanding of seasonal SOM variations may be improved by continuing the sampling of the five vegetation areas examined for additional summer seasons. Additional sampling seasons would also allow for statistical analysis of the seasonal variations to be performed.

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Appendix A

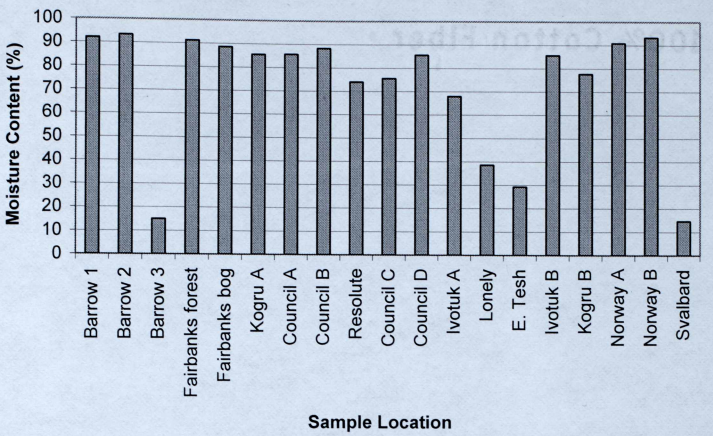

Figure A1: Moisture Content of Incubated Soils

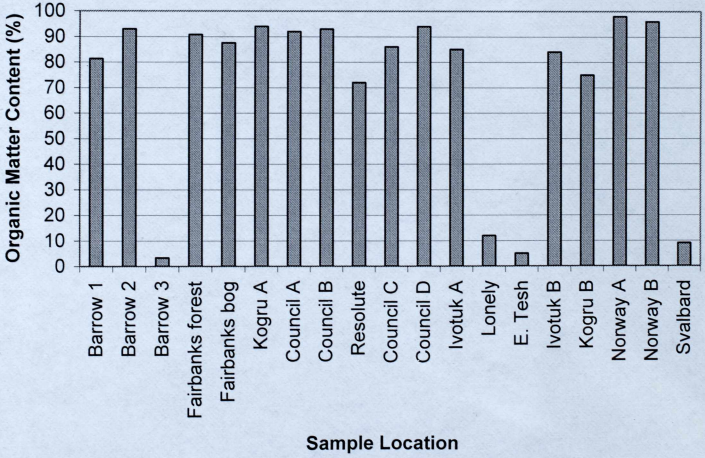

Figure A2: Organic matter content of incubated soils. Calculated as a weight percent.

Table A1: pH values of soils used in incubations.

Soil	pH
Barrow 1	5
Barrow 2	4.5
Barrow 3	5
Fairbanks forest	5
Fairbanks bog	5
Kogru A	4.5
Council A	4.5
Council B	4.5
Resolute	5
Council C	4.5
Council D	4.5
Ivotuk A	4.5
Lonely	7
E. Tesh	6.5
Ivotuk B	4.5
Kogru B	5
Norway A	4.5
Norway B	4
Svalbard	5
China	5

Figures A3-A21 show incubation pressure versus time for each sample incubation performed in the model building experiment.

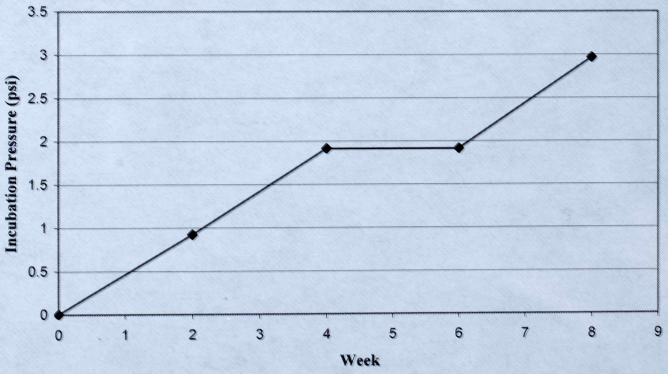

Figure A3: Cumulative incubation pressure for sample Barrow 1.

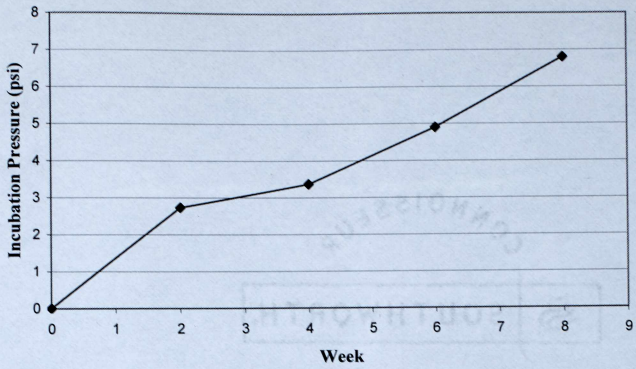

Figure A4: Cumulative incubation pressure for sample Barrow 2.

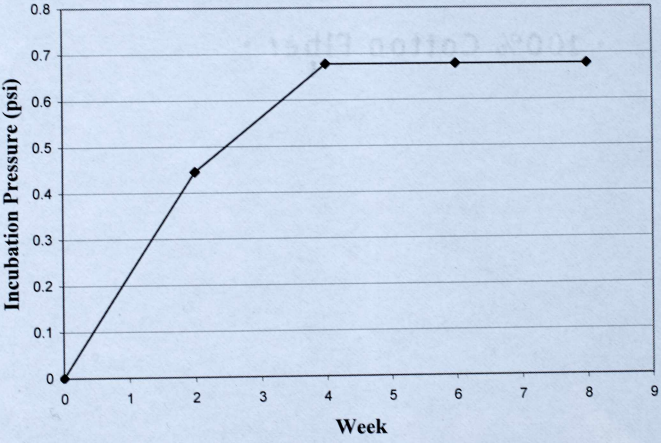

Figure A5: Cumulative incubation pressure for sample Barrow 3.

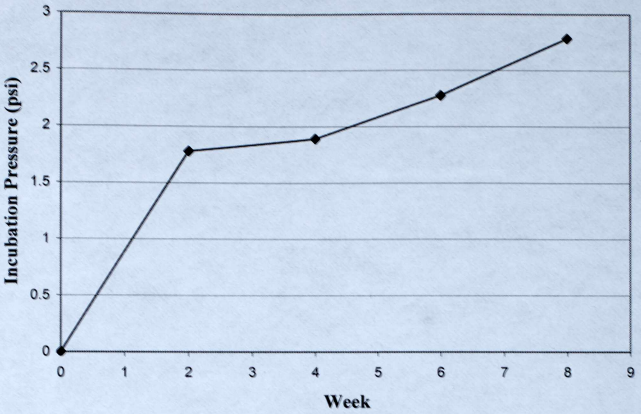

Figure A6: Cumulative incubation pressure for sample Fairbanks forest.

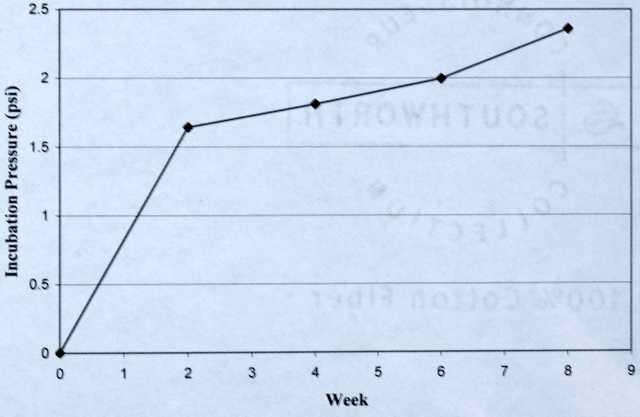

Figure A7: Cumulative incubation pressure for sample Fairbanks bog.

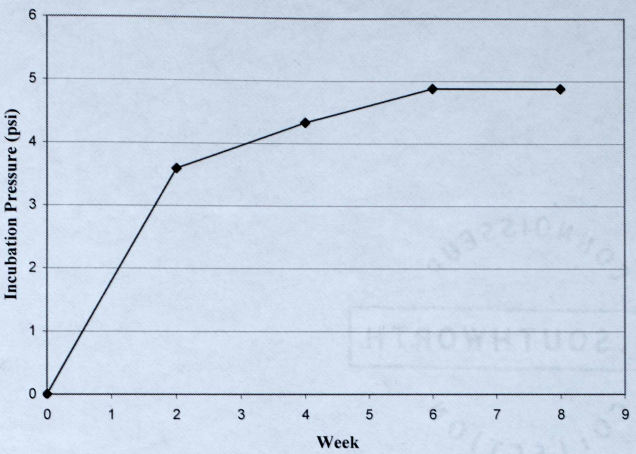

Figure A8: Cumulative incubation pressure for sample Kogru A.

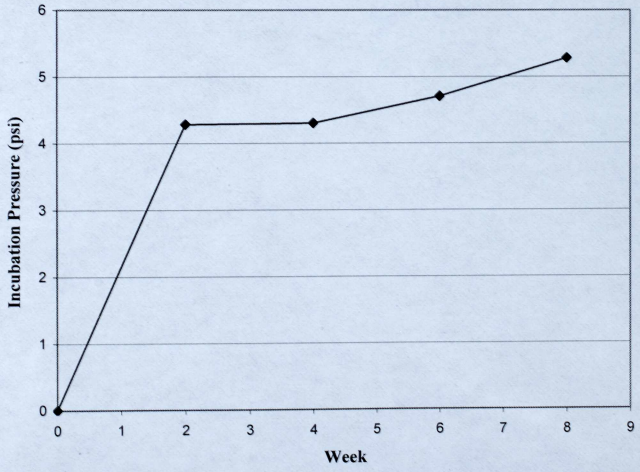

Figure A9: Cumulative incubation pressure for sample Council A.

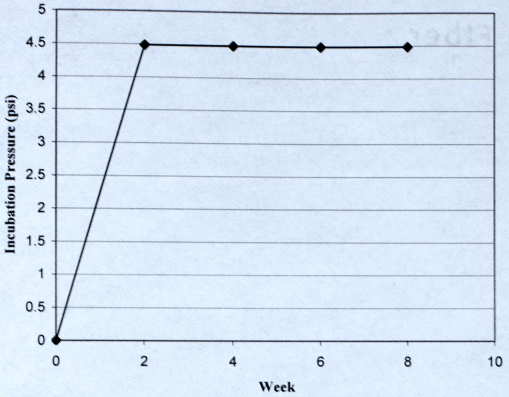

Figure A10: Cumulative incubation pressure for sample Council B.

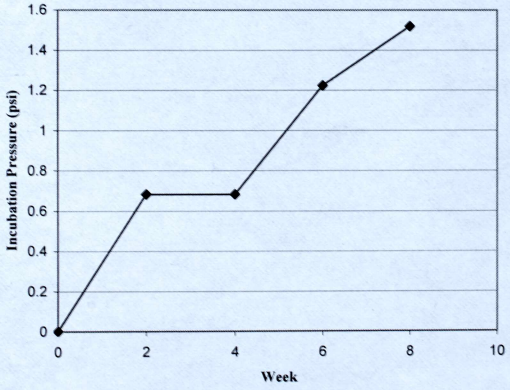

Figure A11: Cumulative incubation pressure for sample Resolute.

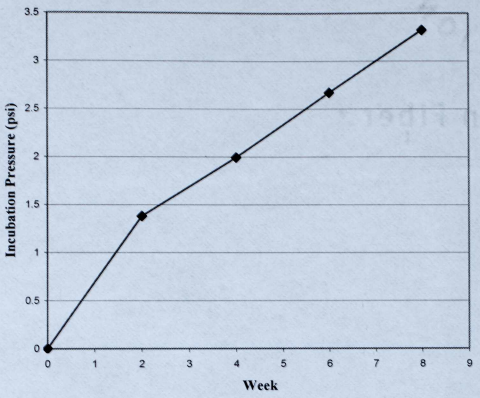

Figure A12: Cumulative incubation pressure for sample Council C.

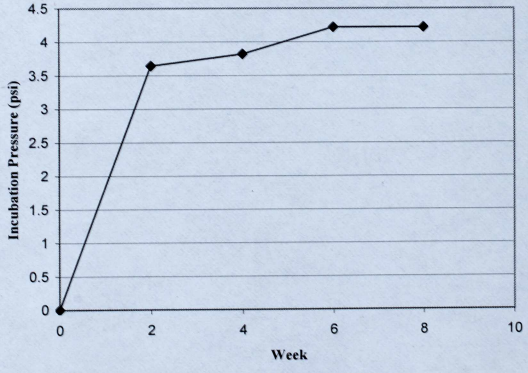

Figure A13: Cumulative incubation pressure for sample Council C.

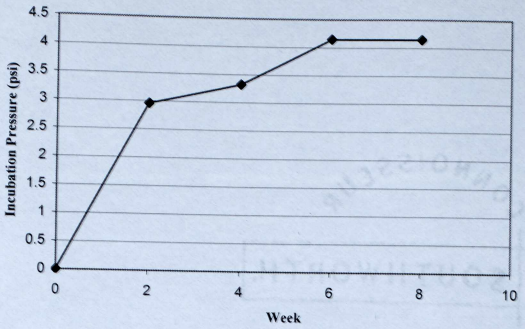

Figure A14: Cumulative incubation pressure for sample Ivotuk A.

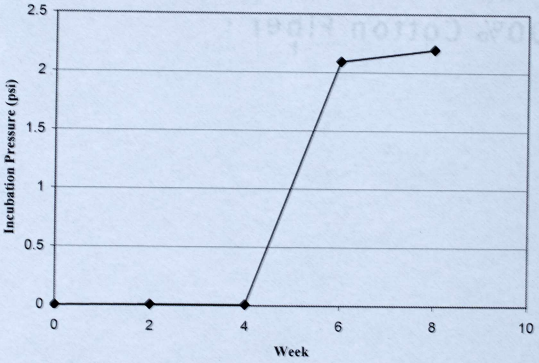

Figure A15: Cumulative incubation pressure for sample Lonely.

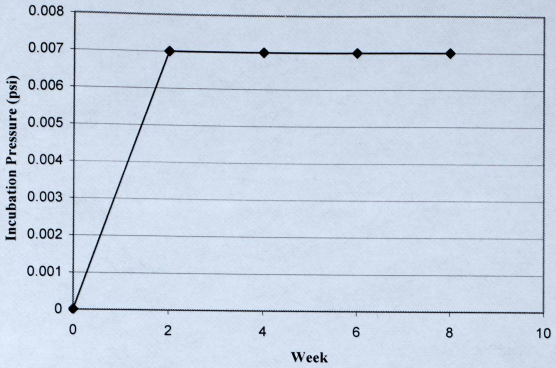

Figure A16: Cumulative incubation pressure for sample E. Tesh.

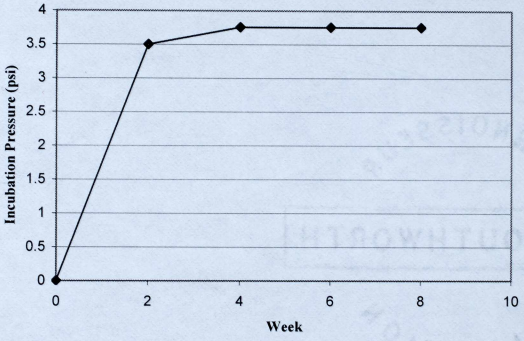

Figure A17: Cumulative incubation pressure for sample Ivotuk B.

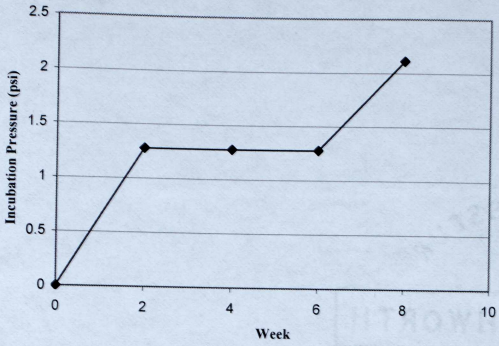

Figure A18: Cumulative incubation pressure for sample Kogru B.

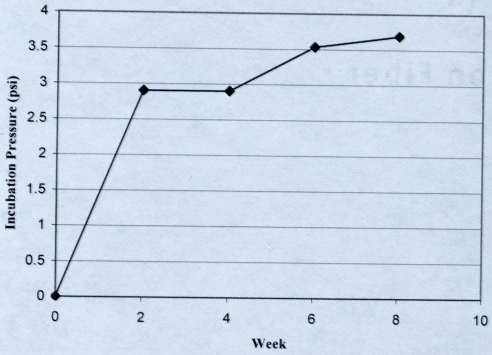

Figure A19: Cumulative incubation pressure for sample Norway A.

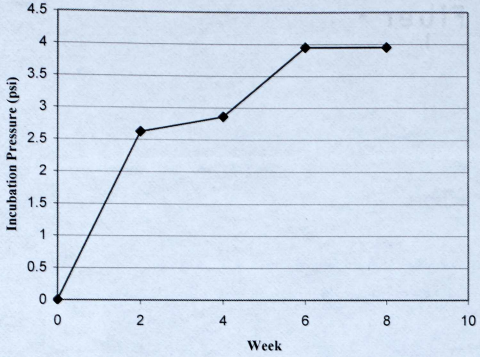

Figure A20: Cumulative incubation pressure for sample Norway B.

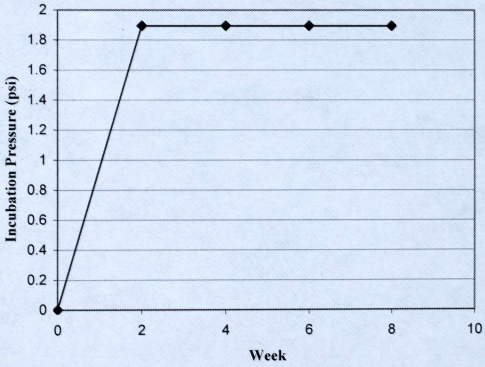

Figure A21: Cumulative incubation pressure for sample Svalbard.

Three full sets of incubations were conducted during the course of this project. The best data set resulted from the final set of incubations, as described henceforth in this paper. A brief description of the initial two incubations will follow in order to provide information for others performing similar experiments. The pressure measurements

performed during the first set of incubations was conducted with a manometer. The pressure in each incubation bottle was normalized to atmospheric after each pressure measurement by allowing air the flow out of the bottle. However, due to changes in ambient atmospheric pressure and the small pressure created by anaerobic respiration, the increase in pressure from one measurement to the next within the bottle was occasionally smaller than the increase in ambient atmospheric pressure, causing air to flow into the bottle when normalized. This introduced oxygen into the incubation, thereby creating aerobic conditions within the bottle. The pressures in the following two incubations were measured with a pressure gauge and without normalizing the pressure between measurements. A number of samples that were incubated showed a decrease in pressure over the course of the incubation. Since anaerobic metabolism creates gas, a decrease in pressure can be attributed to either a loss of gas from the system or a loss of anaerobic conditions through the introduction of oxygen into the system. It was found that incubation of the bottle upside down decreased loss of gas through pierced septa.

Table A2: Actual and alternative minimum pressures measurements.

Week	Sample Location	Actual Pressure (psi)	Alternative minimum pressure (psi)
2	Barrow 1	0.922	0.922
2	Barrow 2	2.724	2.724
2	Barrow 3	0.445	0.445
2	Fairbanks forest	1.78	1.78
2	Fairbanks bog	1.641	1.641
2	Kogru A	3.594	3.594
2	Council A	4.284	4.284
2	Council B	4.483	4.483
2	Resolute	0.683	0.683
2	Council C	1.377	1.377
2	Council D	3.645	3.645
2	Ivotuk A	2.956	2.956
2	Lonely	0.008	0.008
2	E. Tesh	0.007	0.007
2	Ivotuk B	3.501	3.501
2	Kogru B	1.276	1.276
2	Norway A	2.901	2.901
2	Norway B	2.622	2.622
2	Svalbard	1.894	1.894
4	Barrow 1	1.914	1.914
4	Barrow 2	3.364	3.364

Table A2: (continued)

4	Barrow 3	0.678	0.678
4	Fairbanks forest	1.892	1.892
4	Fairbanks bog	1.81	1.81
4	Kogru A	4.333	4.333
4	Council A	4.303	4.303
4	Council B	3.997	4.483
4	Resolute	0.64	0.683
4	Council C	1.994	1.994
4	Council D	3.818	3.818
4	Ivotuk A	3.321	3.321
4	Lonely	0.005	0.008
4	E. Tesh	0.004	0.007
4	Ivotuk B	3.755	3.755
4	Kogru B	1.154	1.276
4	Norway A	2.796	2.901
4	Norway B	2.861	2.861
4	Svalbard	1.465	1.894
6	Barrow 1	0	1.914
6	Barrow 2	4.901	4.901
6	Barrow 3	0	0.678
6	Fairbanks forest	2.275	2.275
6	Fairbanks bog	1.995	1.995
6	Kogru A	4.878	4.878
6	Council A	4.707	4.707
6	Council B	0.007	4.483
6	Resolute	1.223	1.223
6	Council C	2.67	2.67
6	Council D	4.219	4.219
6	Ivotuk A	4.145	4.145
6	Lonely	2.091	2.091
6	E. Tesh	0.003	0.007
6	Ivotuk B	0.004	3.755
6	Kogru B	0	1.276
6	Norway A	3.53	3.53
6	Norway B	3.949	3.949
6	Svalbard	0.003	1.894
8	Barrow 1	2.966	2.966
8	Barrow 2	6.797	6.797
8	Barrow 3	0.101	0.678
8	Fairbanks forest	2.783	2.783
8	Fairbanks bog	2.358	2.358
8	Kogru A	0.013	4.878
8	Council A	5.279	5.279
8	Council B	0.027	4.483
8	Resolute	1.519	1.519
8	Council C	3.322	3.322

Table A2: (continued)

8	Council D	3.424	4.219
8	Ivotuk A	3.819	4.145
8	Lonely	2.195	2.195
8	E. Tesh	0.01	0.007
8	Ivotuk B	0.164	3.755
8	Kogru B	2.111	2.111
8	Norway A	3.69	3.69
8	Norway B	3.695	3.949
8	Svalbard	0.01	1.894

Appendix B

Table B1: SOM pyrolysis GC/MS results of soils incubated. 1PS = primary polysaccharide, 2PS = secondary polysaccharide; PP = polypeptide; PH = phenolic precursor; Alk = alkanes; naph = naphthalene; Cyc = Cyclopentanones

Sample Location	1PS	2PS	PP	LG	PH	LP	Alk	naph	Cyc
Barrow 1	0.302	0.135	0.037	0.170	0.270	0.012	0.027	0.010	0.037
Barrow 2	0.394	0.191	0.024	0.121	0.210	0.008	0.019	0.001	0.032
Barrow 3	0.199	0.036	0.194	0.007	0.352	0.011	0.078	0.068	0.056
Fairbanks forest	0.337	0.030	0.070	0.168	0.196	0.021	0.166	0.009	0.042
Fairbanks bog	0.616	0.082	0.060	0.022	0.027	0.020	0.096	0.008	0.074
Kogru A	0.476	0.099	0.013	0.066	0.279	0.020	0.025	0.007	0.016
Council A	0.539	0.145	0.015	0.043	0.185	0.021	0.024	0.009	0.020
Council B	0.504	0.143	0.014	0.049	0.211	0.022	0.027	0.011	0.020
Resolute	0.264	0.066	0.051	0.126	0.377	0.019	0.036	0.011	0.051
Council C	0.435	0.100	0.022	0.066	0.260	0.032	0.050	0.014	0.022
Council D	0.506	0.123	0.012	0.057	0.238	0.018	0.022	0.007	0.015
Ivotuk A	0.540	0.143	0.013	0.027	0.157	0.037	0.048	0.013	0.022
Lonely	0.192	0.063	0.046	0.105	0.340	0.061	0.122	0.021	0.051
E. Tesh	0.147	0.061	0.042	0.074	0.360	0.082	0.149	0.023	0.062
Ivotuk B	0.551	0.152	0.016	0.037	0.178	0.017	0.023	0.008	0.019
Kogru B	0.324	0.062	0.020	0.112	0.312	0.062	0.077	0.009	0.021
Norway A	0.528	0.125	0.006	0.042	0.245	0.015	0.020	0.005	0.014
Norway B	0.598	0.153	0.006	0.029	0.184	0.007	0.008	0.004	0.010
Svalbard	0.312	0.100	0.059	0.033	0.304	0.031	0.082	0.034	0.045

Graphs of the SOM compound class fractions of index for each soil incubated are shown in individual graphs in Figures B1-B19.

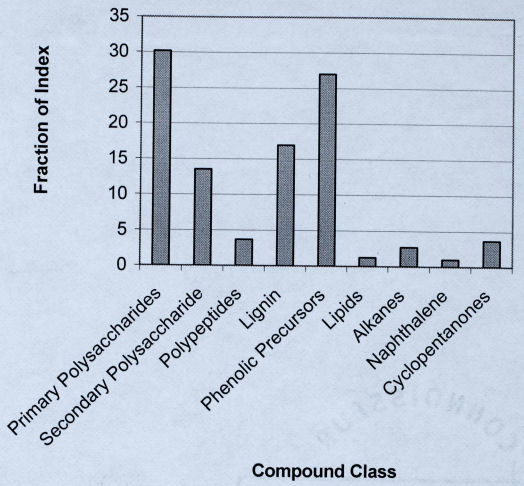

Figure B1: SOM compound class fraction of index for sample Barrow 1.

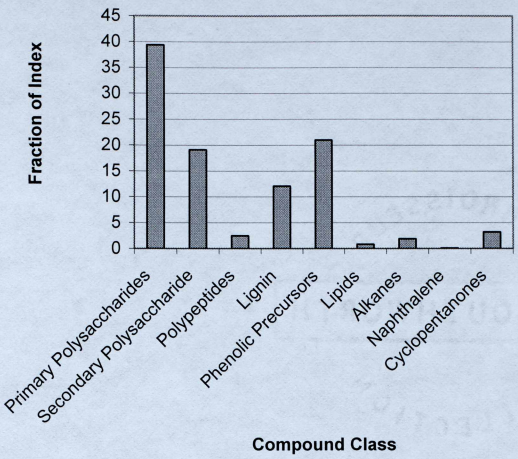

Figure B2: SOM compound class fraction of index for sample Barrow 2.

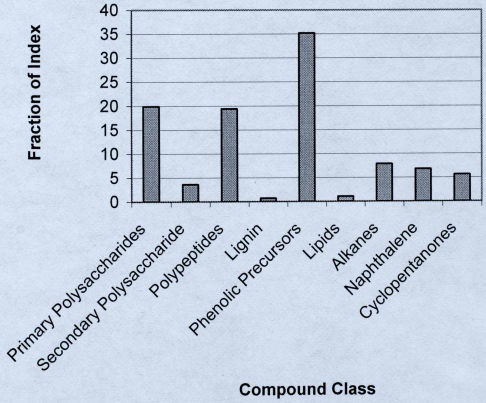

Figure B3: SOM compound class fraction of index for sample Barrow 3.

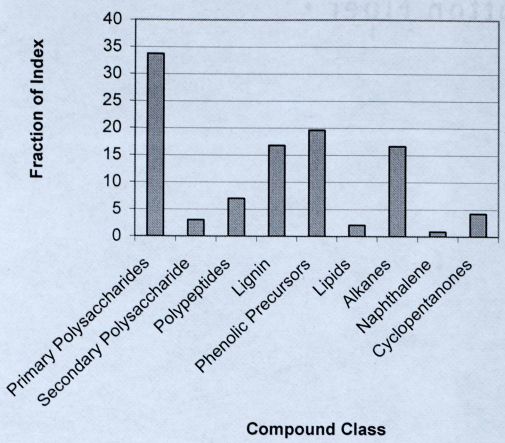

Figure B4: SOM compound class fraction of index for sample Fairbanks Forest.

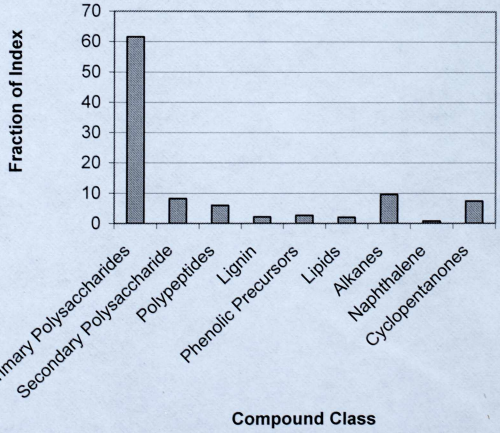

Figure B5: SOM compound class fraction of index for sample Fairbanks Bog.

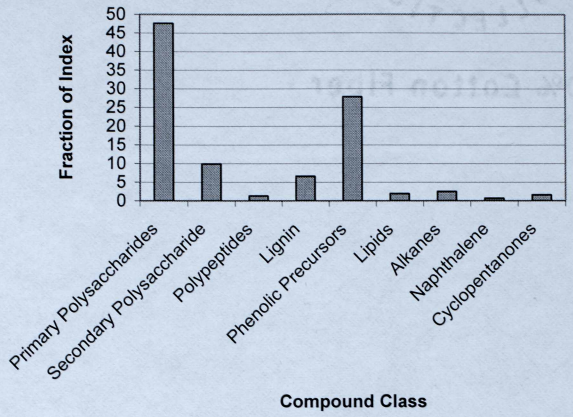

Figure B6: SOM compound class fraction of index for sample Kogru A.

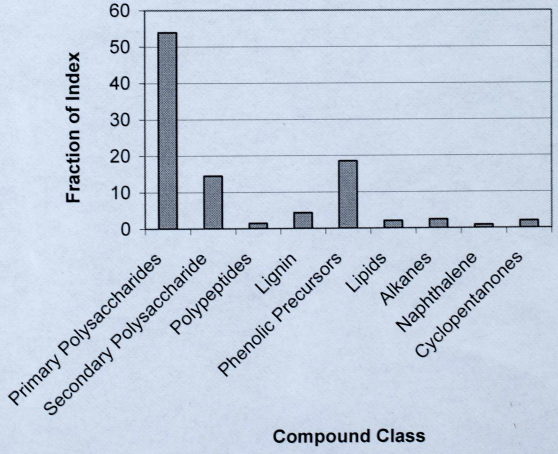

Figure B7: SOM compound class fraction of index for sample Council A.

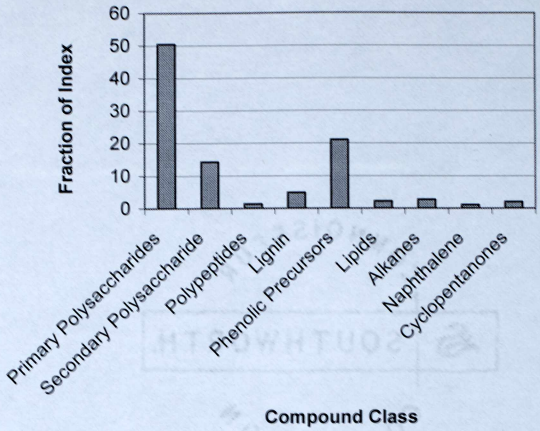

Figure B8: SOM compound class fraction of index for sample Council B.

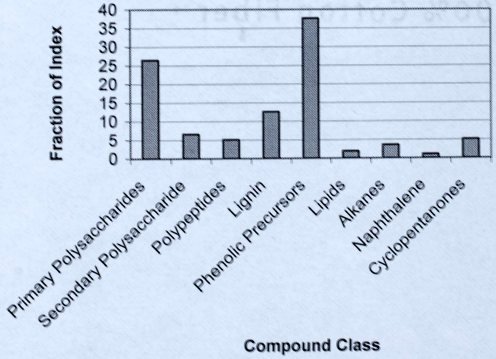

Figure B9: SOM compound class fraction of index for sample Resolute.

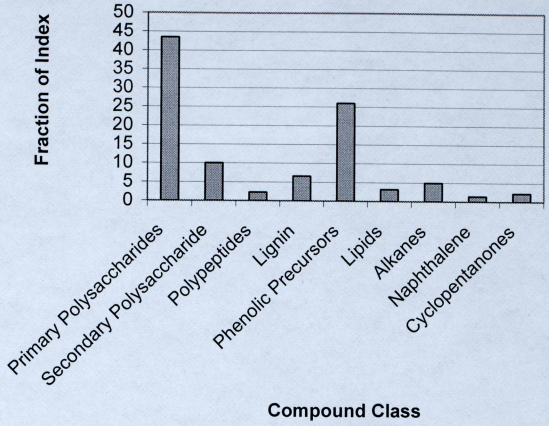

Figure B10: SOM compound class fraction of index for sample Council C.

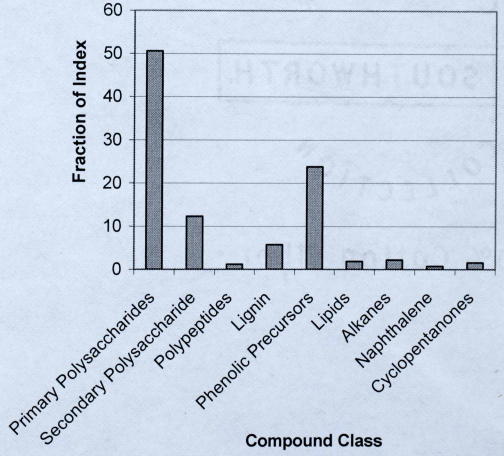

Figure B11: SOM compound class fraction of index for sample Council D.

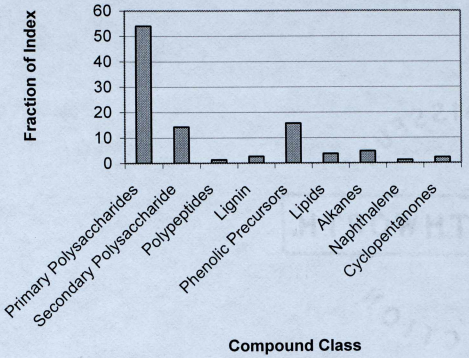

Figure B12: SOM compound class fraction of index for sample Ivotuk A.

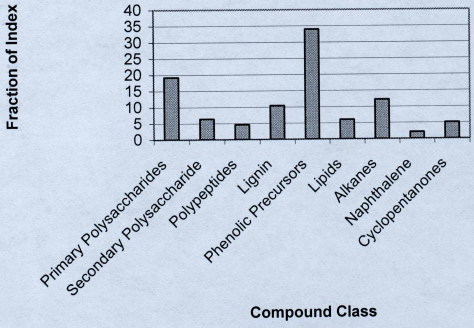

Figure B13: SOM compound class fraction of index for sample Lonely.

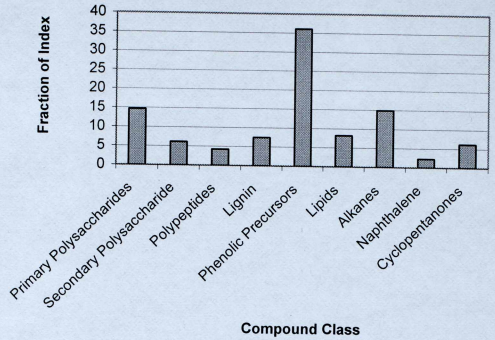

Figure B14: SOM compound class fraction of index for sample E. Tesh.

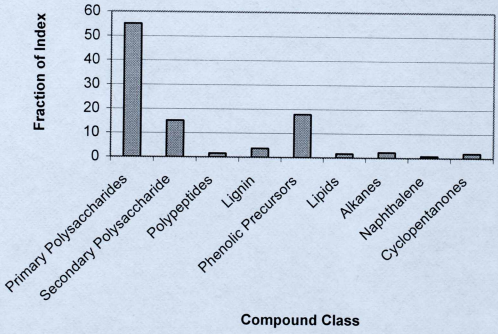

Figure B15: SOM compound class fraction of index for sample Ivotuk B.

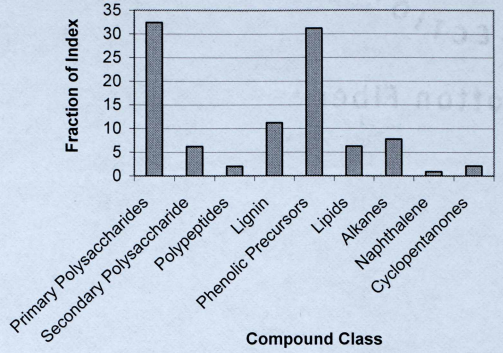

Figure B16: SOM compound class fraction of index for sample Kogru B.

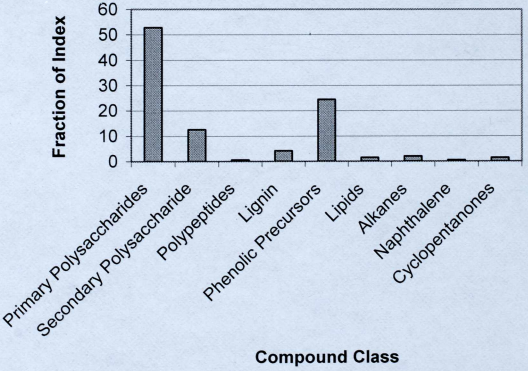

Figure B17: SOM compound class fraction of index for sample Norway A.

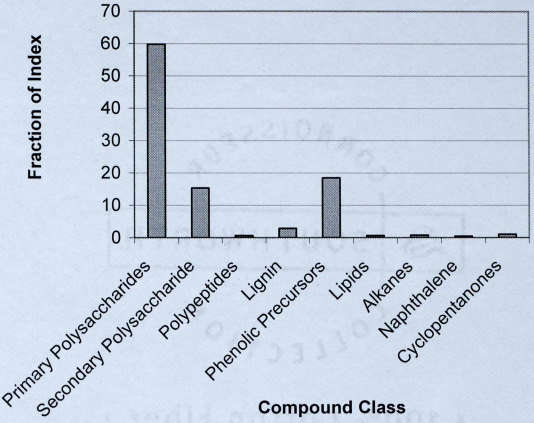

Figure B18: SOM compound class fraction of index for sample Norway B.

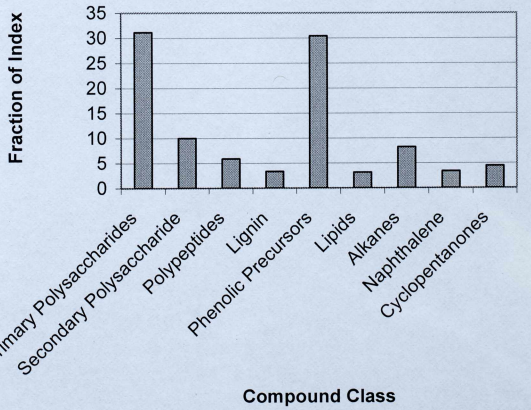

Figure B19: SOM compound class fraction of index for sample Svalbard.

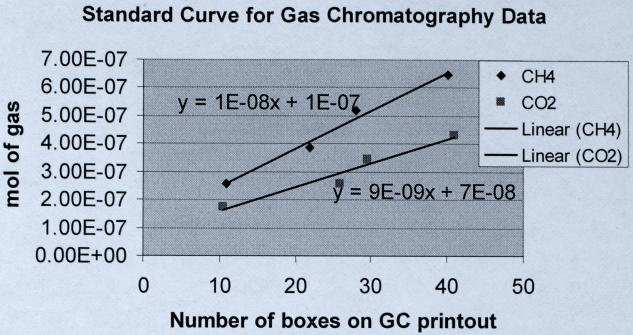

Figure B20: Standard Curves used to calculate molar volume of samples run on the gas chromatograph.

Appendix C

Derivation of the cumulative predicted anaerobic gas production over the course of a summer season (see Figure 28).

Model output = μmol gas/g organic carbon-two weeks-section

μmol gas/g organic carbon-two weeks-section * grams organic carbon/g dry soil = μmol gas/g dry soil-two weeks-section

μmol gas/g dry soil-two weeks-section * grams dry soil/gram wet soil = μmol gas/gram wet soil-two weeks-section

μmol gas/gram wet soil-two weeks-section * grams wet soil in section / cross sectional area of core = μmol gas/ m^2-section-two weeks

μmol gas/m^2-section-two weeks * 1wk/14 days = μmol gas/m^2-section-day

Σ μmol gas/m^2-section-day for each section in core = μmol gas/m^2 day

μmol gas/m^2day * Time between current and last sampling period = μmol gas/m2 sampling period

μmol gas/m^2-sampling period + μmol gas/m^2 sampling period of previous sampling dates = micromol/m^2 cumulative